

AM 1934
hop
c.i

Boston University
College of Liberal Arts
Library

THE GIFT OF

the Author

578.744

BO

AM 1934

hope
c.p.

P7855

BOSTON UNIVERSITY
GRADUATE SCHOOL
Thesis
POTENTIOMETRIC TITRATIONS
THE USE OF PLATINUM ELECTRODES AND
CONSTANT READING POTENTIOMETER CIRCUITS

by

John Hall Hopkins
(Sc.B., Dickinson College, 1932)

submitted in partial fulfillment of the
requirements for the degree of
Master of Arts

1934

H E L

YACHTING HOTELS

ASBESTOS CLOTHING

100 p7855

200 ASBESTOS CLOTHING 100 p7855
300 ASBESTOS CLOTHING 100 p7855

400 100 p7855
(100 100 100 100)

500 100 p7855
600 100 p7855
700 100 p7855
800 100 p7855
900 100 p7855
1000 100 p7855

ASCOLI

OUTLINE

	Page.
I. INTRODUCTION.	1.
II. THEORY OF CELLS AND ITS APPLICATION TO POTENTIOMETRIC TITRATIONS.	6.
III. METHODS.	14.
A. Classical methods.	14.
B. Titration to zero difference in potential.	21.
C. Polarized indicator electrode.	22.
D. Electrode system consisting of two metallic electrodes.	23.
E. Differential titration.	24.
F. Fields of research.	28.
IV. ELECTRODE SYSTEMS CONSISTING OF TWO METALLIC ELECTRODES.	29.
A. Work of Willard and Fenwick.	29.
a. Bimetallic systems.	
b. Polarized platinum electrodes.	
B. Work of VanName and Fenwick.	39.
C. Other metallic systems.	44.
D. Note. List of reactions followed by the system of Willard and Fenwick.	49.

MINUTO

1882

I

COLONIALISTI X

3

OT INITIATIONE ETI UNA CAVO NO INCONTRARE
ACCIDENTALMENTE

41

BOCCIONI III

51

abortion license II

61

Initiation in connection with the initiation

79

abortion license bill

81

bill for the initiation of the abortion

83

abortion

91

initiation license bill II

99

bill to allow the initiation of the

INITIATION OUT TO UNIVERSITIES AND COLLEGES VI

101

SECURITY

109

allowing the initiation to know a

different initiation

abortion initiation bill

111

allowing the initiation to know a

different initiation bill

bill to allow the initiation to know a

124

allowing the initiation to know a

V. CONTINUOUS READING DEVICES.	51.
A. Galvanometry.	51.
B. Electron tube circuits.	54.
a. Goode's apparatus.	55.
b. Partridge's apparatus.	56.
c. Apparatus of Kassner, Hunge and Chatfield.	58.
VI. EXPERIMENTAL RESULTS.	61.
A. Preliminary work.	61.
B. System of Willard and Fenwick.	66.
C. System of Foulk and Bawden.	75.
D. Polarization Phenomena.	77.
E. System of Kassner, Hunge and Chatfield.	80.
F. Burette Electrode.	82.
SUMMARY.	84.
BIBLIOGRAPHY.	86.

Electrometric titrations are of two general types, conductometric and potentiometric. As the name suggests, the basis for the first is the change of electrical conductivity of the solution as the reacting solution is added. In the second type, one titration electrode is used in a chemical half-cell by the precipitation into the solution of a suitable electrode. By observing the voltage change during the titration, the course of the reaction may be followed.

Digitized by the Internet Archive
in 2017 with funding from
Boston Library Consortium Member Libraries

POTENTIOMETRIC TITRATIONS
THE USE OF PLATINUM ELECTRODES AND
CONSTANT READING POTENTIOMETER CIRCUITS

I. INTRODUCTION.

The use of electrometric titrations is one of the most important of the recent developments in the field of quantitative chemical analysis. The extensive research of the past fifteen years in the use of electrometric methods has given to analytic chemistry a large amount of information of both theoretic and practical interest and importance.

The theoretic basis for electrometric methods of analysis is found in the electrolytic dissociation theory of Arrhenius and the mass action principle, as applied to ionic equilibria. (1)

Electrometric titrations are of two general types, conductimetric and potentiometric. As its name suggests, the basis for the first is the change of electrical conductivity of the solution as the reacting solution is added. In the second type, the titration chamber is made a chemical half-cell by the introduction into the solution of a suitable electrode. By following the voltage change during the titration, the course of the reaction may be followed.

(1) H. S. Taylor, *A Treatise on Physical Chemistry*, 2nd. ed., D. Van Nostrand Co., New York, 1931, Vol. 2, p. 901.

The scope of this thesis is limited to a very small part of the potentiometric titration field.

Fundamentally, titrating potentiometrically consists of the determination of the change in voltage characteristic as the reaction is carried out, of the cell formed by the solution and a suitable electrode. There are many methods of forming this cell, depending upon the type of electrodes used. The type of electrode used depends upon the nature of the system. There are, too, many methods of measuring the voltage. The choice of the method of measuring the voltage depends upon the electrodes used and the nature of the system, although the standard potentiometer system is applicable to nearly all electrode systems. Many of the electrode systems are difficult to use and require an expert technician to make and operate. The measurement of the voltage accurately and efficiently, in many methods, requires expensive and extensive equipment. It is the constant objective, therefore, of research to experiment towards simpler methods, more efficient and practical because of less tediousness in manipulation.

The importance and value of this type of analysis can be readily shown by a short survey of its uses and advantages. In general, it can be used for almost any reaction which can be titrated by the usual methods and for all of the most important and well known reactions. The uses of potentiometric titrations are rapidly and constantly increasing in number

as research brings forth new electrodes and new equipment. This is evidenced by the fact that the literature in this field between 1926 and 1930 is as extensive as for the period between 1892 and 1926. (1)

In research laboratories, whether theoretic, medical or industrial, it is found valuable in all volumetric analysis. By special adaptation, it is found valuable to the medical laboratory in determining hydrogen ion concentration of the body fluids, and to the theoretic laboratory, as a method of interpreting reactions in terms of ionic concentrations and activities.

Its uses in industry are too extensive to attempt a complete list. The following list gives a rough picture of the extent and versatility of its use: acidity in milk, metallic plating solutions, solutions for the treatment of leather, wool scouring liquids, paper sizing, water purification and sewage disposal processes. (2)

The development of constant reading devices has brought a new tool to industry, not only for use in the laboratory but also in the actual processes. The electrodes may be placed in the pipe lines or reaction vessels and the concentrations of the reactants accurately determined and controlled.

In titrating colored or cloudy solutions, where a

- (1) N. H. Furman, Ind. Eng. Chem., Analyt. Ed., 2, 213 (1930)
(2) H. C. Parker, Ind. Eng. Chem., 19, 660 (1927)

colorimetric indicator change would be difficult to see, or in reactions requiring outside indicators, its advantage over the usual methods is obvious. In the ordinary colorimetric methods it is necessary to make a correction for the difference between the colorimetric end-point and the true equivalence-point. This correction is primarily for the amount of reagent necessary to react with the indicator and to give to the solution color of intensity enough to be detected. In the case of acid-base titration, since few of the ordinary indicators change color at the equivalence-point, another correction is needed. The need for these corrections is eliminated by the use of potentiometric titrations.

The chief disadvantages of this method are the length of time necessary for titration and the extensive amount of equipment used. It is to be noted, however, that with the latest developments, have come the constant reading devices, the use of which makes the time for potentiometric titration as short as for the regular titration, and for some reactions, much shorter. The simplification of equipment, too, has brought into use apparatus which is far less expensive and less difficult to operate.

It is the object of this thesis to study through the scientific literature and, in a more limited manner, in the laboratory some of the latest developments in this field, with a view to determining their adaptability to routine work in

to see if this will be done by the members of the
new organization and if the existing organizations will
contribute to it. It is also proposed to have a
conference on the subject at the end of the year.
The conference will be held in New York City in
December and will be organized by the American
Federation of Labor and the National Education
Association. The purpose of the conference is to
discuss the problems of education and labor and
to find ways and means of cooperation between
the two. The conference will be opened by a
speech by Dr. John Dewey, president of the
American Federation of Labor, and will be
followed by a discussion of the problems of
education and labor. The conference will be
closed by a speech by Dr. John Dewey, president of the
American Federation of Labor, and will be
followed by a discussion of the problems of
education and labor.

laboratory. As the title indicates, the use of platinum electrodes and constant reading devices are the problems of major interest. In the field of platinum electrodes, the polarized system and the burette electrode are of special interest. The simpler galvanometer systems as well as electron tube circuits will be studied.

Dissertation, and the book "The Determination of Hydrogen Gas", by F. M. Clark, (1) (2)

As it was stated in the introduction, the principle of potentiometric titration is the formation of a half-cell by the immersion into the solution of the proper electrode, thereby causing the change in voltage characteristic of the half-cell, during the titration the course of the reaction may be followed.

The most fundamental half-cell consists of a small platinum plate immersed with a solution of its ions. The tendency of the metal to go into solution is called the standard solubility pressure. The opposing pressure is the vapor pressure of the ions in form molecular form. When an electrode of this type is placed in contact with standard, a reaction occurs depending upon the difference between the hydrolytic solution pressure and the vapor pressure of the ions. If the solution pressure is greater than that of

- (1) E. M. Goldhoff and H. H. Faraday, *Potentiometric Titration*, 2nd. ed., John Wiley and Sons, New York, 1931.
- (2) F. M. Clark, *The Determination of Hydrogen Gas*, 3rd. ed., Williams and Wilkins Co., Baltimore, Md., 1928.

•
-self amitely to see off members of its off za
-team to spending all the social parties instances his robust
-bentley and especially himself to knit off nL
-and -faster friends to the shopself offered and the many
-atmosphere and morale as flew as many a testimony to his
-abilities and illus

II. THEORY.

It is advisable at this point to discuss briefly the theory underlying the principle of potentiometric titration. For a complete theoretic explanation of this subject, the reader is referred to "Potentiometric Titrations", by I. M. Kolthoff and N. H. Furman, and the book "The Determination of Hydrogen Ions", by W. M. Clark. (1) (2)

As it was stated in the introduction, the principle of potentiometric titration is the formation of a half-cell by the introduction into the solution of the proper electrode. By determining the change in voltage characteristic of the half-cell during the titration the course of the reaction may be followed.

The most fundamental half-cell consists of a metal electrode placed in contact with a solution of its ions. The tendency of the metal to go into solution is called the electrolytic solution pressure. The opposing pressure is the osmotic pressure of the ions to form molecular form. When an electrode of this type is placed in contact with its solution, a reaction occurs depending upon the difference between the electrolytic solution pressure and the osmotic pressure of the ions. If the solution pressure is greater the metal goes

- (1) I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931.
- (2) W. M. Clark, The Determination of Hydrogen Ions, 3rd. ed., Williams and Wilkins Co., Baltimore, Md., 1928.

est yliedun uonish or shioq eitd to viderivis si fi
noitidis ofitesdinteg to elisiong est goylabaw xroba
est jeeqas eitd to noitidis qidetisdi viderivis a tor a
M. I vd "noitidis ofitesdinteg" of viderivis si tider
to noitidis "est" kood est has meant H. I has thondiX

(S) (I) KISIO M. W vd "anoI negoyih
to elisiong est noitidis eitd nk baste aw di aA
vd fleo-flel a te noitidis est si noitidis ofitesdinteg
shortsle roqig est to noitidis est qid noitidis est
est to ofitesdinteg eyatlov ni egnsa est ymilitateh vd
ya noitidis est to satus est noitidis est ymilit fleo-flel
bewollai ed

Iade a te avianos fleo-flel fethabni tson est
est , andi est to noitidis a dliw dosjao si bessiq shortsle
-oje est ballec si noitidis andi og of iade est to yenebni
-so est si excessing galioune est . excessing noitidis oiflor
ne new . grof infocion grof of andi est to excessing oiflor
noitidis est dliw dosjao si bessiq si eyt eitd to shortsle
est neated konstilid est noq yahaseh tson noitidis a
to excessing oiflor est hta excessing oiflor cityforfe
seen Iade est raters ar excessing noitidis est H. I , andi est

anoitidis ofitesdinteg hont H. I has thondiX M. I (I)
the 5rd andi negoyih to noitidis ofitesdinteg eye Gisio M. I (S)
the 5rd andi negoyih to noitidis ofitesdinteg eye Gisio M. I (S)

into solution in the ionic form. This involves leaving upon the electrode a negative charge, an electron. If the osmotic pressure is greater, the metal goes out of solution, involving the gain of an electron from the metal electrode. This reaction will continue until the two electrolytic pressures are equal. The electrolytic solution pressure is constant for the metal electrode but the osmotic pressure of the ion varies with the ionic concentration.

If a method is devised to carry off the electrons from the electrode in the first case or to furnish electrons to the electrode as in the second case, in some continuous manner a current will be drawn from the half-cell and the reaction will be continuous until one of the reactants is gone.

This electrode reaction is represented by:



M represents the metal, M^n represents the ion. $n\theta$ gives the number of electrons reacting per ion.

The voltage characteristic of this reaction is represented by:

$$E = - \frac{RT}{nF} \ln \frac{P}{p} \quad \underline{B.}$$

in which R is the gas constant, T the absolute temperature, n the number of electrons reacting per ion, F the charge on one gram equivalent of an ion (one Faraday 96,500 coulombs); ln represents the natural logarithm. P is a constant for

any given electrode, and represents the electrolytic solution pressure; p represents the osmotic pressure of the ions and varies with the ionic concentration. This equation is a slight modification of the original Nernst equation.

For practical use this equation is further modified:

$$E = e + \frac{0.0591}{n} \cdot 0.0002(t-25) \log c \quad \underline{C.}$$

The constant has been introduced from the relationship between the p of equation B. and the ionic concentration c at 25 degrees centigrade, and the change to the decadic logarithms. .0002 is the value for R divided by F . The e represents the constant for the voltage pressure of the P of equation B.

For complete accuracy the c should be multiplied by the proper activity coefficient since the theoretic equation holds true only when the activity of the ion is used. However the activity and the concentration are often nearly the same in value. Furthermore, the determination of the activity is still a rather undeveloped field and many of the individual activities are not accurately known. For work in potentiometric titration the use of the concentration gives sufficient accuracy.

There is another mathematical function of concentration which is widely used especially in hydrogen ion work. It is usually signified by a small p written with the symbol of the ion concerned. Represented mathematically:

$$p_{\text{ION}} = -\log c_{\text{ION}} \quad \underline{D.}$$

and the other districts and communities has a critical situation.
His position to give an efficient and independent government
to the West and the South is determined right but his policy
of force cannot be justified and it will only
lead to civil war and to the abolition
of the Federal Government which will result in the

9 of December, 1860. — 2 — 2

accused him of being an archabolitionist and a disunionist and
that he is a uncompromising abolicionist & nothing to do with
the cause of freedom and it seems that his principles are
such as those of a man who holds the slaves as God's
people to be fit for the use of master and not subjects
and the abolition of slaves to add to their substance to
add to nothings although all sorts of fellatio offices require
the slaves to work for nothing & nothing is more than they can
eat or drink & when held in slavery there is no civil or
moral obligation to them but they are to be treated like
slaves & nothing but the most degrading treatment
is to be done to them and though they are not
so bad as to hold them by force but to hold them
in such a way so as to be able to do nothing
but to do what they are told to do & to do it
as well as they can & to do it as well as
they can & to do it as well as they can &
nothing but to do it as well as they can &
nothing but to do it as well as they can &
nothing but to do it as well as they can &
nothing but to do it as well as they can &

100 100 — 100

In order to use this function, equation C. is modified to read:

$$E = e + \frac{0.591}{n} 0.0002(t-25) \text{ pION } E.$$

There is no method known of measuring the voltage of a single half-cell directly. It is necessary to form a complete cell. This is done by combining the half-cell, to be determined, with another half-cell of known and constant voltage. The internal connection is usually made with a salt bridge. Having now a complete cell, the total voltage may be measured by any one of the many methods available. The voltage of the unknown half-cell is found then from the equation:

$$E.M.F. = E_{ref} + E = E_{ref} + e + \frac{0.591}{n} 0.0002(t-25) \text{ pION } E.$$

This equation indicates that the voltage measured, E.M.F., is the algebraic sum of the voltages on the two half-cells, written in the order electrode-solution/solution-electrode, according to the accepted conventions concerning the cell. There is a small voltage incurred at the liquid junction but this is so small that it is omitted in potentiometric titration work. This set-up is shown diagrammatically in Figure 1.

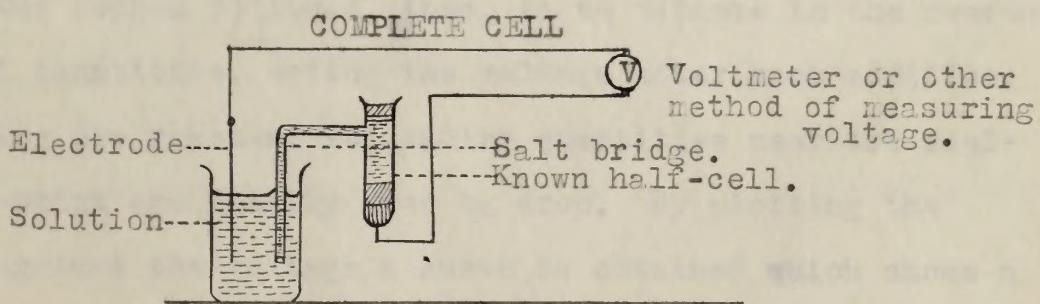


Figure 1.

The methods of measuring the voltage of the cell will be discussed in the next part of this thesis.

It has been shown that the voltage on the electrode in a solution of its ions is a function of the concentration of the ions.

There are three types of reactions used in volumetric analysis: neutralizations, precipitation reactions and oxidation-reduction reactions.

In the neutralization and precipitation reactions, the ion, upon whose concentration the potential depends is changed by the reactant to form a relatively unionized compound. This change in concentration of the ion changes the potential and since this change is greatest near the equivalence-point a break is found in the titration curve.

In oxidation-reduction systems the ratio of the oxidant to the reductant which governs the potential on the indicator electrode. As this ratio changes the potential will change. As the equivalence-point is approached one of the members of the ratio will approach a very small value and the change will be greater causing a break in the titration curve.

The method followed, then, is to titrate in the reactant in small quantities, noting the voltage after each addition, and adding the reactant in smaller quantities near the equivalence-point and finally drop by drop. By plotting the volume against the voltage a curve is obtained which shows a

decided break at the equivalence-point. This break corresponds to the number of milliliters of reagent equivalent to the amount of the ion present in the sample being titrated. Another method of determining the equivalence-point is to calculate $\frac{\Delta E}{\Delta c}$ for each addition of the reagent. $\frac{\Delta E}{\Delta c}$ is the ratio of the potential change with the amount of reagent added. By plotting $\frac{\Delta E}{\Delta c}$ against the volume of reagent added a curve is obtained which shows a maximum at the equivalence-point. By using $\frac{\Delta E}{\Delta c}$ the equivalence-point may be determined without the use of a graph, since for the drop at the equivalence-point, this value will be greatest.

Figures 2 and 3 show the titration curves for a typical acid-base titration. The titration equivalence-point is easily detected.

TITRATION CURVE
HCl-NaOH

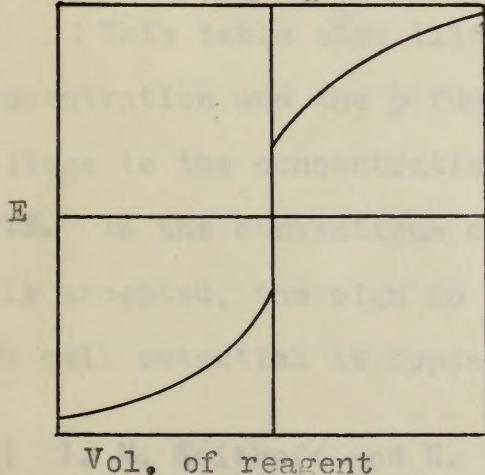


Figure 2. E plotted against volume

TITRATION CURVE
HCl-NaOH

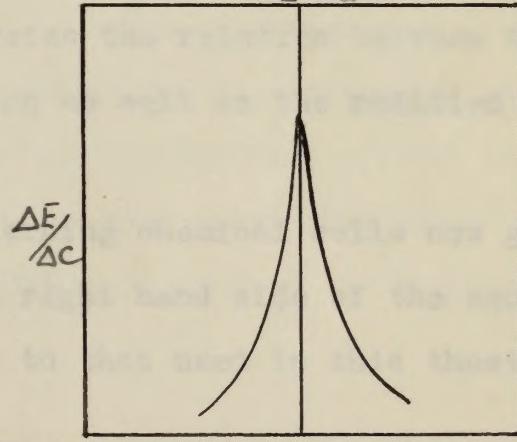


Figure 3. $\frac{\Delta E}{\Delta c}$ plotted against volume.

To illustrate even more clearly, Table I. is presented showing the change in voltage with the concentration and the value $\frac{\Delta E}{\Delta C}$. (1)

TITRATION OF HCl WITH NaOH.

Percent neutralized	$[H^+]$	pH	E_{H_2}	$\frac{\Delta E}{\Delta C}$
0	10^{-2}	2	$e+2x.059$	
90	10^{-3}	3	$e+3x.059$	65
99	10^{-4}	4	$e+4x.059$	
99.9	10^{-5}	5	$e+5x.059$	
100	10^{-7}	7	$e+7x.059$	1180
Excess				
.1	10^{-9}	9	$e+9x.059$	1180
1	10^{-10}	10	$e+10x.059$	
10	10^{-11}	11	$e+11x.059$	65

Table I.

This table also illustrates the relation between the concentration and the p function as well as the relation of voltage to the concentration.

NOTE. In the conventions concerning chemical cells now generally accepted, the sign in the right hand side of the equation for cell potential is opposite to that used in this thesis.

(1) I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931. p. 29.

III. METHODS.

In the preceding section the basic theory of potentiometric titration has been discussed briefly. It is this theory which laid the foundation for the method known as the classical method. The operation of this classical method will be presented followed by a review of the developments in methods in the whole field.

The review is based upon the report and review of progress by N. H. Furman. (1) For complete information, the reader is referred to "Potentiometric Titrations" by I. M. Kolthoff and N. H. Furman, and "The Determination of Hydrogen Ions", by W. M. Clark. (2) (3)

The Classical Method.

Figure 4 presents diagrammatically the apparatus and set-up for use in the classical method. (4)

This method makes use of an indicator electrode in a solution to be titrated, and a reference electrode, of constant and known potential. By titrating in portions of the reactant and determining the voltage between the electrodes after each addition as explained in the foregoing section the course of the reaction is followed.

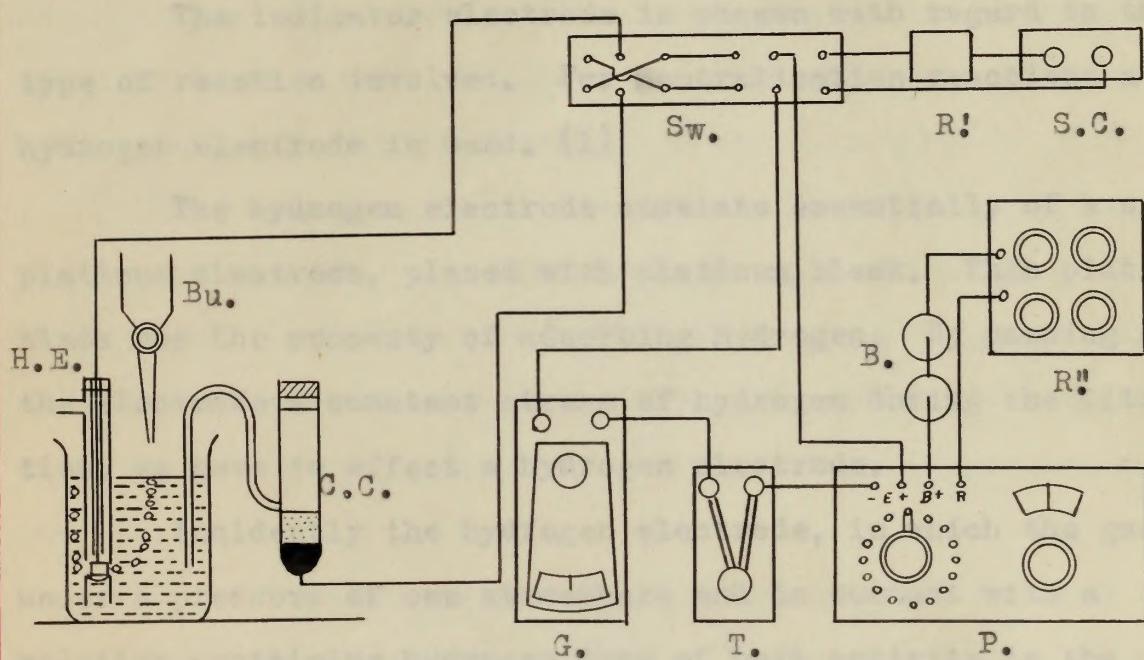
- (1) N. H. Furman, Ind. Eng. Chem., Analyt. Ed., 2, 213 (1930).
- (2) I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd. ed., John Wiley and Sons, New York, 1931.
- (3) W. M. Clark, The Determination of Hydrogen Ions, 3rd. ed., Williams and Wilkins Co., Baltimore, Md., 1928.
- (4) I. M. Kolthoff and N. H. Furman, op. cit., p. 94.

-elmeleg to vident cased eft noidee gaiberg ent al
 vident sind si tl . vident beausch used and noitritit oridem
 Isciasdo ent as award horden ent tol noidee to ent bief horden
 -erq ed iflw horden Isciasdo sind to mordrege ent . horden
 ni ebogen ni etmolevah ent to weiver s vd bewoiffel bejne
 ,biefi sfodn ent
 -erq to weiver has droet ent doog heasd si weiver ent
 ent ,biefi siflentia intorlation mle (f) ,biefi H . W vd mord
 M . I vd "aniditit cintorlation" od horden si reber
 negev to Determiantion to Hydron and ,biefi H . K has Giflony
 (z) (s) ,biefi M . W vd "aniditit"

,horden Isciasdo ent
 and amrugg eft vleektemergete ammecti A emgitt
 (A) ,horden Isciasdo ent ni ean tol qn-tec
 s ni shortcele roccibni us to ean sclem horden aidt
 jutisces to shortcele sonerter s has heaffit ed of noilfors
 jutisces ent to amrugg ni qn-uritit vd . Iskineg amrugg has
 nose rafir seborcele ent neewed sytlov ent yamireter has
 to eamc eft horden grigore ent ni benidicke as noitrib
 ,bewoiffel si noicest ent

(oset) gis S . bW . tylAn ,mec ,hnl ,Tun ,Cp ,hnl ,Tun ,H . W (I)
 anot ritit cintorlation ,biefi H . W ,biefi H . W ,biefi H . W (S)
 ,biefi H . W (C)
 ,biefi H . W (z)
 ,biefi H . W (s)

CLASSICAL METHOD OF POTENTIOMETRIC TITRATION



- S.C. Standard cell.
- R' High resistance to protect S.C.
- Sw. Switches.
- R'' Variable resistance.
- B. Dry cells.
- P. Student potentiometer
- T. Tapping key.
- G. Galvanometer.
- C.C. Calomel cell or other reference electrode.
- Bu. Burette.
- H.E. Hydrogen electrode or other indicator electrode.

Figure 4. (1) Hydrogen electrode used as a small platinum electrode. (2)

The most successful type is a small bright platinum wire. This electrode has been found capable of following an oxidation-reduction reaction.

- (1) Dr. Potentiometric Titrations, Rothberg-Foxon, p. 256.
- (2) Determination of Hydrogen Ions, Clark, p. 254.
- (3) Potentiometric Titrations, Rothberg-Foxon, p. 256.

The equivalence-point is determined by one of the methods mentioned.

The indicator electrode is chosen with regard to the type of reaction involved. For neutralization reactions a hydrogen electrode is used. (1)

The hydrogen electrode consists essentially of a small platinum electrode, plated with platinum black. This platinum black has the property of adsorbing hydrogen. By passing over the electrode a constant stream of hydrogen during the titration, we have in effect a hydrogen electrode.

Incidentally the hydrogen electrode, in which the gas is under a pressure of one atmosphere and in contact with a solution containing hydrogen ions of unit activity is the standard for the electrode potential for all electrodes.

The use of the hydrogen electrode is a simple example of the fundamental theory of the cell. The potential on the electrode varies with the concentration of the hydrogen ion. Table 1 and Figures 2 and 3 show the result typical of this type of titration.

In an oxidation-reduction reaction, the indicator electrode usually used is a small platinum electrode. (2) The most successful type is a small bright platinum wire. This electrode has been found capable of following an oxidation-reduction reaction.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 200.
Cf. Determination of Hydrogen Ions, Clark, p. 221.

(2) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 45, 254.

•BE
-em ent zo sno yg besluiteseb si jolcq-concluips enT

benoijnes aboij
ent od preyer nijw noono si shortoile tofscibn enT

s amidosec noitssifatuem roT svjovni noitcoet lo eqy

(1) .bean si shortoile negoribn

lisa s lo vlijnnesse abaiaco shortoile negoribn enT
muntelb. sidT .noitcibn dtil befeib shortoile muntelb
tevo gneang yg .negoribn ynlidrosh lo vlijnnesse enT ned zom
-erit enT olnkoh noono si metje instance s shortoile enT

shortoile negoribn a jocilie ni enT enT enT
si smg enT olnkoh si shortoile negoribn vlijnnesse

a dtil jocilie ni huc studijante sno lo stucessg s raba
ent si vlijnnesse sim lo sno i negoribn gainlaano noitulos

.shortoile lis roT lalnenoq shortoile enT roT bishnate
elgake elgake s si shortoile negoribn enT lo sno enT

enT no lalnatoe enT .Hlo enT lo vlosit lalnatoe enT lo
noi negoribn enT lo mokterhoscod sno dtil esitev shortoile
enT lo lalnatoe tluor enT woda Z hde Z esugit huc f oldet

negoribn lo eqy

tofscibn enT noitcoet noitcoet-noitcoet noitcoet us ni

(2) .shortoile muntelb lisu s si bean vlijnnesse shortoile
enT .sim amidosec dglid lisu s si eqy lalnatoe roT enT
noitcoet noitcoet noitcoet noitcoet noitcoet noitcoet

*002 *4 0001-Modific moitserit sistemoisatoe .10 (1)

*002 *4 0013 0001-Hlyb to moitserit sistemoisatoe .10

*002 *4 0001-Modific moitserit sistemoisatoe .10 (2)

When a precipitation reaction is to be followed use is generally made of a metal electrode, corresponding to the metallic ion being precipitated. Here is another example of changing of the ion to a substance relatively unionized, thereby lowering the osmotic pressure of the ions. (1)

The precipitation of the silver ion from a solution by the use of a soluble chloride is an example of the type of precipitation reaction. In this case a silver electrode is used to follow the decrease in silver ion concentration. It might be noted that a chlorine electrode might also be used in this titration.

For a reference electrode a half-cell must be used that has a constant and known potential. There are several of these in use. The two most used are the calomel cell and the silver chloride half-cell.

The calomel cell is for most purposes the most practical. It has all of the characteristics essential to the successful half-cell. Its potential is little changed by change in temperature and this change has been accurately measured. It is fairly simple to construct and, when made carefully, gives the theoretic potential reproducably. Barring contamination, it is stable. (2)

Essentially it consists of a small amount of mercury in

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p.9.

(2) Cf. The Determination of Hydrogen Ions, Clark, p. 303.

ai seu bewillt ed of ai noijeset noijigicerg a neu

ed of gajibogaserrt ehotjels ijer = to aben yilrenen
to elanxe terjons ai erre. hafstigicerg ukted noi offisier
-eredt heimotus yfeyteler oomadus a of noi edt to gajibogas

(1) enot edt to sinasing oijomao est gajibogas
yd oijulos s uorl hei tevlie edt to noijigicerg edt

to oqej edt to elanxe us ai shirolo sifulee a to van enj
ai shirjels tevlie a amc uids al noijeset noijigicerg
ti noijatrasence noi tevlie ai eamtech edt wofft od beca
hi been od oela rigi shirjels emtolda s jukt bekor ed Jigia
noijeritj uids

trit beca od hem Ille-tilde a aboutole someter a rof
saent ho larevan ova stort. Leitnader nwoal his dntance a sei
tevlie odt his Ille-tilde edt ova been frot owt edt , van ai

Ille-tilde shirolo
Isoldeitj dof erit eeoduy jec rof ai Ille-tilde edt
eulitaseoca odt of Leitnader oitkiesosido edt to his edt ji
-ust ni egado yd oonalo elstif et leitnader ti Ille-tilde
ai ji , betwenn yfeyteler need ued egado uids his erntse
edt eavie .Uitlero eba oewt apen eba oewt of elgria vtil
ti noijatrasence. Ryddensborger Leitnader oitkiesosidt

(2) uids ai
ai yuotet to tmuas Ille-tilde a to staisace ti yfeyteler

• 9.0. Eojefti-tildejell oitkiesosidt Tijfemjofetj 10 (f)
• 803 • 9.0. The Determiantion of Hydrolou ion Gfis 10 (s)

contact with its salt mercurous chloride, in the presence of a solution of potassium chloride. The potential of the cell varies with the concentration of the potassium chloride solution. It is, therefore, of great importance that the solution of potassium chloride be accurately known concentration. There are three concentrations of potassium chloride which are in general use and for which most of the measurements have been made. They are .1 normal, saturated and the standard, the normal solution. Contact is made with the outside circuit by means of a platinum wire dipping into the mercury but not in contact with any of the other constituents of the cell. The contact with the other half-cell is made by means of a salt bridge usually containing a saturated solution of potassium chloride. If the solution to be titrated contains silver or mercury ions, the salt bridge should be filled with the nitrate or sulphate.

The silver chloride half-cell consists of a silver wire, the surface of which has been coated by electrolytic methods with silver chloride. The silver wire leads to the outside circuit. A solution of potassium chloride surrounds the wire and forms a salt bridge to the solution. This cell has the disadvantage of being light sensitive, so must be used in the dark or mounted in a light proof container. It is difficult to make this cell accurately. In other words the potential is not reproducible. (1)

(1) A. A. Noyes and J. H. Ellis, J. Am. Chem. Soc., 39, 2532 (1917)

It is readily seen that a method of measuring voltage must be used which does not draw current of an appreciable amount from the cell. Although a voltmeter would be the simplest method of measuring the voltage, unless this were in series with a high resistance, current would be drawn from the cell to an amount great enough to cause considerable error. The standard method of measuring the voltage is to make use of the potentiometer system. (1) A simple form of the potentiometer system is shown diagrammatically in Figure 5.

SIMPLE POTENTIOMETER SYSTEM

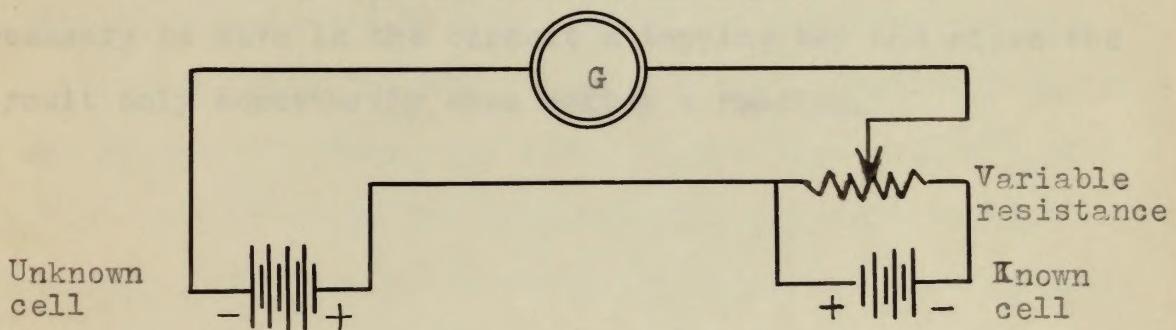


Figure 5.

In a few words, the theory of this electrical circuit is to oppose the voltage to be measured with an equal voltage. When this condition exists a galvanometer in the system will read zero showing that no current is passing. The opposing potential is varied with a resistance. By measurement of the resistance necessary to balance the unknown potential, the unknown potential may be determined. For this purpose the resistance is usually calibrated and used with a known cell.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 84.

The potentiometer apparatus used in potentiometric titrations is included in Figure 4. In this apparatus a specially calibrated resistance or potentiometer is used, so that when the potentials balance the potentiometer reads the voltage directly. The source of opposing current is from dry cells, which have been calibrated against a standard cell such as the Weston cell. This calibration is necessary at the beginning and end of each titration. The potentiometer system minimizes the amount of current taken from the solution, but it is necessary to have in the circuit a tapping key and close the circuit only momentarily when making a reading.

new potential between the electrodes. This method eliminates the necessity of using the galvanometer system. A suitable instrument, such as a galvanometer or millivoltmeter, is available at the beginning of each titration.

Pickard¹ and Fossell² developed this system by their own time but independently. By using a galvanometer or a low sensitive voltmeter in series with a high resistance, Fossell was able to take this system beyond reading.

While this system is very nice, it is intricate and costly. It has the decided disadvantage of necessitating a different electrode system for each titration. The difficulty in compensating for the effect of foreign electrolytes in the solution due to the effect of temperature makes for inaccuracies.

[1] E. H. Pickard, Jour. Phys. Chem., Analyst., Vol. 2, No. 2, 113.
[2] G. Fossell, Potentiometric Titrations, Research Dept., 14-15.

58

-is oljekontinenzon bi þau enniðagð vefsíðanum sif
vilkunum á enniðum síðum n. A. Því er til fáhlöglar til hafið
máluð dæir os þau til nafnolindar og til ónnarleiðar fastalindar
spjótar og ekki nafn nafnolindar eit stórlíða skrifstofu og til
vilkunum yfir með til fáhlögum til sögnar sif. Vilkunin
eit en hóp líka bréfbaða - tannar - bogstöfla með svæfi þáttu
gildingar eftir til vefsíðan til nafnolindar sif. Líka með
-kínun meðvæg fáhlindar sif. Nafnolindar eru til þau
bi til fæð enniðum eit með ónnarleiðar fáhlögum til fáhlöglar og
eft skoð eru vefsíðan yfir með fáhlögum eft af ónnarleiðar
fáhlögum til vefsíðan með vefsíðum yfir með fáhlögum

There are four other fundamental methods of potentiometric titration: titration to zero difference in potential; polarized indicator electrodes; electrode system consisting of two metallic electrodes; and differential titration. Each is a special modification of the classical method. (1)

Titration to Zero Difference in Potential. (2)

This system is constructed by substituting for the standard calomel cell a reference electrode of potential identical to that of the titration solution and its electrode at the equivalence-point. The equivalence-point is marked, then, by a zero potential between the electrodes. This method obviates the necessity of using the potentiometer system. A null point instrument, such as a galvanometer or capillary electrometer, is all of the measuring apparatus necessary.

Pinkhof and Treadwell developed this system at about the same time but independently. By using a galvanometer or simple but sensitive voltmeter in series with a high resistance, Treadwell was able to make this system constant reading.

While this system is very simple in operation and cost, it has the decided disadvantage of necessitating a different electrode system for each titration. The difficulty in compensating for the effect of foreign electrolytes in the solution and for the effect of temperature makes for inaccurate

(1) N. H. Furman, Ind. Eng. Chem., Analyt. Ed., 2, 213, (1930)
 (2) Cf. Potentiometric Titrations, Furman-Kolthoff, p. 95.

results.

Mlle. Brouchere has modified this system slightly, for use in metallic ion determination. Using two identical electrodes, one in the unknown solution and the other in a known solution, she forms a complete cell. The solution of known concentration is more dilute than that of the unknown concentration. By titrating into the unknown solution pure water, the concentration of the two may be made identical. At this point the voltage between the two will be zero. The disadvantages of the original system are inherent to this system.

Müller measures the potential of the equivalence-point and uses this value to oppose the potential of the titration cell. This is another modification of the null-point method. The difficulty of making the potential equivalence-point measurements, makes this system unsatisfactory. There are, too, other influences which make the equivalence-point potential vary even in consecutive titrations.

Polarized Indicator Electrodes.(1)

It is inadvisable in some cases to use a metal corresponding to the ion in solution as an electrode. Dutoit and vonWeisse devised the polarized electrode for the purpose of replacing this electrode. A platinum electrode is polarized cathodically by means of a small polarizing electrode carrying a small current. The platinum indicator electrode is kept

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.

plated with a light layer of the metal giving it the characteristic potential of the metal in question. This system, while applicable to a few titrations, is essentially inaccurate due to the loss in metal by the plating from the solution.

Electrode System Consisting of Two Metallic Electrodes.(1)

In this system, both the indicator electrode and the reference electrode are replaced by metallic electrodes, both of which are in the unknown solution. In one variation of this method two platinum electrodes are used given different potentials by means of a low polarizing current. In the other the two electrodes are of dissimilar metals, which have been found capable of following the reaction to be studied. Both systems are essentially the same in theory.

The simplicity of this system in the preparation of the electrodes is an advantage. The danger of diffusion error, characteristic to the use of any type of salt bridge is eliminated. The ease with which this system can be used when an inert atmosphere is necessary for the titration is another important advantage. It is not possible to measure oxidation-reduction potentials directly or pH values with this system. In fact the potentials may vary from titration to titration, due to the effect of the preparation of the electrode. It is

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.

found, however, to be an accurate method of titration, since it is not the absolute potential, which is in this case important but the relative values in the one titration. It should be noted that some metallic electrodes have been found which can be used for pH values and similar work, but in general this system is not applicable to such work.

Much of the recent research has been done in this field. Its practical advantages and the high degree of accuracy with which the titration may be made by this system make it of fundamental importance.

Since this field is the major subject of this thesis, it will be presented thoroughly in the next section.

Differential Titration. (1)

This system is another which is characterized by a high degree of accuracy. In ease of use, however, it is second to the bi-metallic system, since in most differential titration methods, special apparatus is used which requires experience to operate.

In this system two metallic electrodes are used, usually of the same metal and often platinum. One of the electrodes is in contact with the main body of the solution and the other is placed in a small portion of the solution isolated mechanically from the main body of the solution. This causes a difference in potential between the electrodes which is at a

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 112.

maximum at the equivalence-point. The titration curve of this system resembles that of the $\frac{\Delta E}{\Delta c}$ curve of the classical method.

D. C. Cox seems to have been the first to introduce this method. His method involves the titration of aliquot portions of the unknown solution simultaneously. The solutions are contained in separate beakers and connected by means of a salt bridge. The reacting solution is run in by means of two burettes. The total amount run into the first is kept at a constant amount greater than that run into the second by about .1 to .2 milliliters. The electrodes used are two platinum electrodes, one in each solution. The potential between these two electrodes will be different and have a maximum difference when the first has reached the equivalence-point.

This system has many advantages. It is very accurate. It eliminates the necessity of plotting curves. Diffusion troubles incident to the use of the salt bridge are eliminated since both solutions so connected are of nearly the same concentration.

MacInnes and his co-workers have done much work in modifying the work of Cox. In general their system is to have both electrodes in the one container. A small portion of the solution is isolated from the rest of the solution mechanically and is in contact with one of the electrodes. After the addition of a portion of the reagent, there is a difference of potential between the electrodes due to the fact that they

are in solutions of different concentration. After making the reading of the voltage, the isolated portion of the solution is mixed with the rest before another addition of the reagent is added. This procedure is carried up to the equivalence-point, at which point the electrodes will have the greatest difference in potential.

These modifications eliminate the use of two burettes, are simpler to operate, yet just as accurate.

The latest apparatus by MacInnes and Dole (1) is worthy of note for its simplicity and for its ingenious apparatus. It is shown diagrammatically in Figure 6. The glass shield isolates part of the solution surrounding the one electrode. The isolated portion of the solution is mixed with the rest, when necessary by means of a gas lift pump. The burette stopcock is so constructed that it regulates the supply of gas to the lift pump as well as admitting the reagent. When the reactant is being added to the main portion of the solution, no gas can flow. By turning the stopcock one-eighth turn, the reagent is cut off as well as the gas. The reading is now made. By completing a quarter turn from open, the gas is allowed to flow mixing the isolated portion with the rest of the solution.

The burette electrode (2) is usually included in this field although its titration curve is not similar to those of

(1) D. A. MacInnes and M. Dole, J. Am. Chem. Soc., 51, 1119(1929)
(2) H. Willard and A. W. Boldyreff, J. Am. Chem. Soc., 51, 471(1929)

the regular differential titration. It is shown in Figure 7. It is simple in construction, yet accurate in results. A small platinum wire is sealed into the tip of the bureete below the stopcock. This forms a half-cell with the reagent solution and thereby serves as a reference electrode. The indicator electrode is usually a platinum wire. The tip of the burette is placed under the surface of the solution to be titrated and acts as a salt bridge. It has been found experimentally that there is no appreciable diffusion error. This may be accounted for by the fact that the reagent is flowing into the solution most of the time during the titration.

DIFFERENTIAL TITRATION
APPARATUS

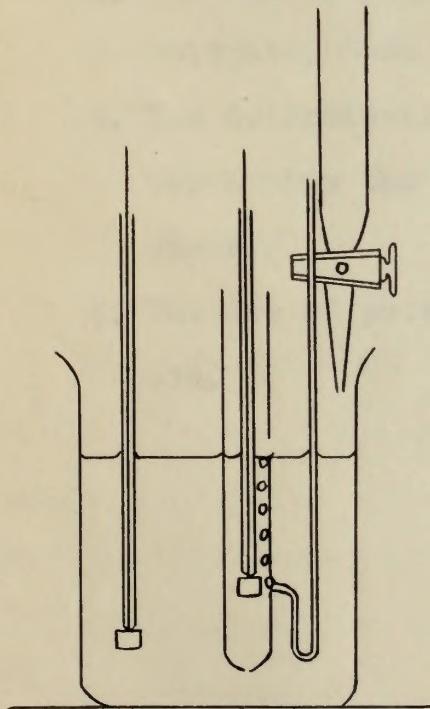


Figure 6. Apparatus of
MacInnes and Dole.

THE BURETTE
ELECTRODE

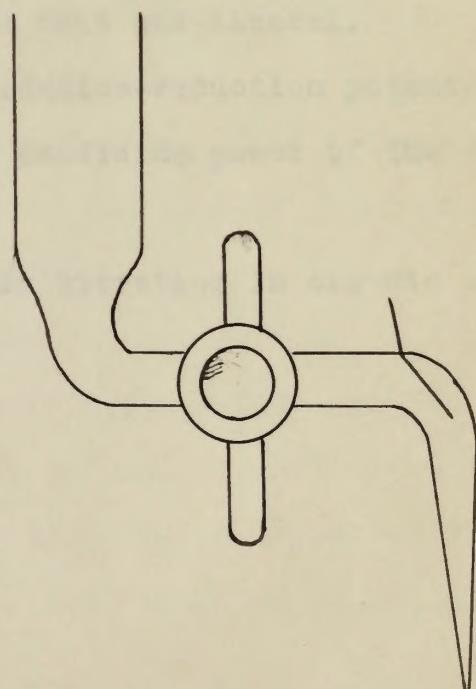


Figure 7.

Since the interest of this thesis is one of method, a resume of most of the important methods has been given before the discussion of the one system chosen for study.

It is of interest also, to list other fields of research in potentiometric titrations and its special modifications. (1)

1. Determination of pH at which quantitative reactions take place most efficiently. (Not necessarily volumetric)
2. Potentiometric micro-titration.
3. Development of new electrodes, especially for use in neutralization reactions.
4. The use of potentiometric titrations in non-aqueous solvents, such as acetic acid and alcohol.
5. The determination of oxidation-reduction potentials, which show the relative oxidizing power of the reagents.
6. The use of potentiometric titration in organic analysis.

(1) N. H. Furman, Ind. Eng. Chem. Analyt. Ed., 2, 213, (1930)

IV. BIMETALLIC ELECTRODE SYSTEMS.

This system of potentiometric titration was mentioned in the last section. The simplicity of this system was pointed out, as well as the various advantages connected with its use.

Hostetter and Roberts, while investigating the use of a palladium electrode as an indicator electrode in an oxidation-reduction reaction, found that the voltage between it and a half-cell remained almost constant throughout the titration and no break was observed at the equivalence-point. (1)

F. Müller has shown that this behavior is true only of such reactions in hydrochloric acid solutions and is due to surface change in the metal. (2)

The discovery of this unique action of palladium, however, suggested a complete study of the metallic electrode systems for use in potentiometric titrations.

Willard and Fenwick and later VanName and Fenwick made extensive investigation in this field and much of the basic work was contributed by their research.

Willard and Fenwick first took up the problem in 1920. They first verified the work of Hostetter and Roberts. (3) A strip of palladium was used for a reference electrode and a platinum wire for an indicator electrode. A sharp but transient equivalence-point was found. The transient nature of

(1) J.C. Hostetter and H.S. Roberts, *J. Am. Chem. Soc.*, 41, 1337 (1919)

(2) F. Müller, *Z. Elektrochem.*, 34, 237 (1928)

(3) H.H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, 44, 2504 (1922)

benelijkoen new politieke oordeningen te slaven en
bedienen niet voldoende zijn te verschillen van de politieken die tot nu
toen ook welke bediening te voorzien heeft dat de volkeren een
te hoge mate van arbeid en leed hebben en dat de arbeiders
niet meer dan een aantal dagen en nachten kunnen werken en
dat de arbeiders een aantal dagen en nachten kunnen werken.

(2). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te velen enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(3). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(4). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(5). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(6). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(7). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(8). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(9). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(10). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

(11). Tijdens een reis door de Verenigde Staten ontmoette ik een Amerikaan die
te veel enig te verkeerde ideeën had over de arbeiders en de arbeiders-

the break with the palladium made its use as a reference electrode unsatisfactory. In further investigation they found that even the first break came after the equivalence-point, causing considerable error. By reducing the surface of the palladium, the error was lessened but the operation was still unsatisfactory. It was found that this property of palladium is characteristic of oxidation-reduction reactions in which a quantity of strong hydrochloric acid is present. In dilute hydrochloric acid solutions or in sulfuric acid, no break was found in a titration curve. The conclusion was made that the palladium was attacked, which caused the presence of another reducing agent besides the one being titrated.

An alloy of gold and palladium was tried, but the results obtained were irregular and too high. A platinum-palladium alloy electrode was then used. In this case, too, evidence of attack on the palladium was apparent.

The best results were obtained with a small wire of platinum-palladium in place of the foil previously used. It was found that even this showed signs of attack after several titrations.

The work with palladium suggested that other metals might give better results and extensive investigation was started.

In the work with palladium all reactions studied consisted of various solutions of dichromate and ferrous iron. In

the following work the use of permanganate and other oxidants and reductants was also studied.

The system of a platinum indicator electrode and a platinum-rhodium alloy reference electrode was found to give good results. The accuracy was found to depend upon the acidity. In the reaction involving dichromate, solutions containing less than 50% of hydrochloric acid were found to give excellent results, and when sulfuric acid was used 20% seemed optimum. The results in the use of permanganate were slightly irregular.

Because of the resistance to acid action of tungsten, this metal seemed to offer a promising electrode material. Accurate breaks were obtained using the tungsten against both platinum and the regular half-cell and also against the platinum-rhodium alloy electrode. The results were better in the case of the dichromate than with the permanganate. By the addition of manganous sulfate to the solution, it was found that the permanganate could be used with this electrode accurately even in the presence of hydrochloric acid. In all titrations the magnitude of the equivalence-point break was small.

The research was continued using other metals of the unattackable class. Molybdenum, tantalum, iridium, osmium and gold, in combinations of each other, with palladium, with tungsten, with platinum, with platinum-rhodium were all experimented with. The use of platinum alloys of these metals and

other alloys of these metals were tried.

Briefly the investigation showed the following combinations to be the most satisfactory: Pt, Pt-Rh; W, Pt; W, Pt-Rh. All palladium electrodes whether pure or alloys were found to be unsatisfactory.

The character of the bimetallic system is different from that of the ordinary metallic, half-cell system.

Figure 8 shows a characteristic titration curve. It will be noted that the potential read does not vary from a small quantity until very close to the equivalence-point. The equivalence-point is marked by a sharp rise. Tungsten is an exception. Its curve shows a gradual rise during the titration with the characteristic sharp rise at the equivalence-point.

The magnitude of the potential difference at the equivalence-point is less in the bimetallic system than in that involving a half-cell. The magnitude of the bimetallic system break will vary from titration to titration, although it always occurs at the equivalence-point. The magnitude of the break also varies with the method of pre-treatment.

An excess of the oxidizing reagent brings various results. In any combination with platinum, in a solution in which dichromate is used, the potential after the equivalence-point break may rise slightly, fall slightly or remain constant depending upon the amount of acid present. In the reactions involving permanganate a very sharp decrease in potential is found in an excess of the oxidant. In systems

involving tungsten only a slight "crawl" usually to a higher potential is found in an excess of the oxidant.

It was found that the magnitude of the break was greater and sharper when sulfuric acid was used than when hydrochloric acid formed the acid medium.

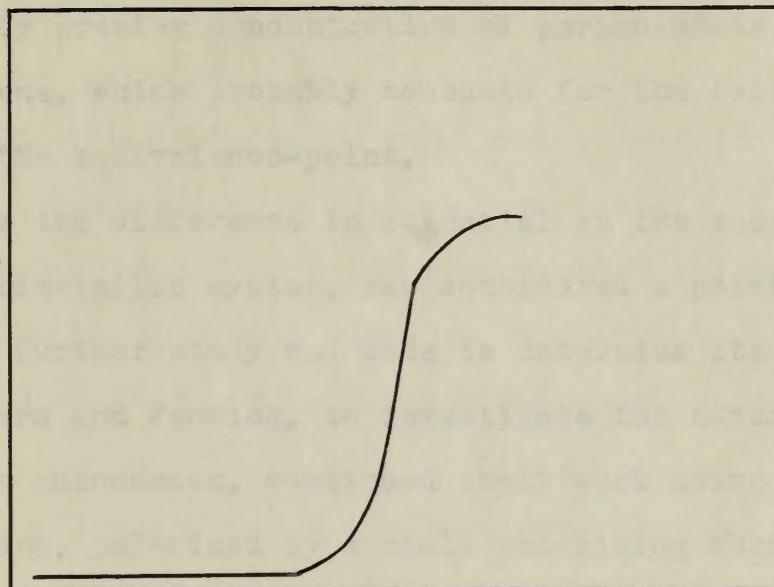
In order to study the equivalence-point phenomenon, a half-cell was also placed in the solution and the system arranged so that throughout the titration the potential on both metallic electrodes could be determined.

Figure 9 shows typical curves resulting from such an experiment. It illustrates clearly the function of the two electrodes. ^{Figure 9}

Initially in the presence of the reducing agent alone, the potential of the two electrodes is different. On the addition of a slight amount of oxidizing agent this difference falls to zero, and remains at that value to within a half a milliliter of the equivalence-point. As the equivalence-point is approached the electrodes begin to function differently, having a maximum difference at the equivalence-point. While this difference always exists at the equivalence-point, its magnitude varies. The individual electrode potential differs too, depending upon their pre-treatment and may change after use. Platinum is normally positive to its alloys and to tungsten. Its polarity may change with its alloys after use. Between platinum and tungsten, however, there is never a reversal of polarity although the difference does vary.

EQUIVALENCE-POINT BREAK WITH BI-METALLIC ELECTRODES

E.M.F.

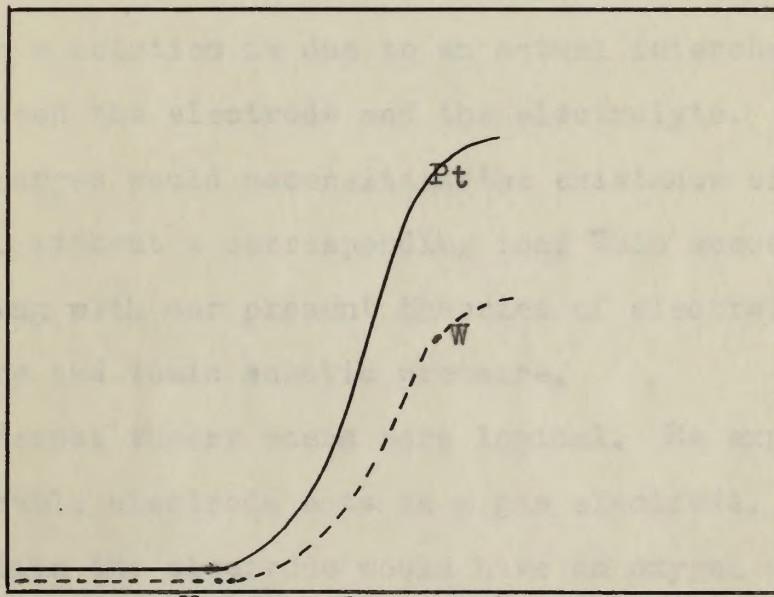


Volume of reagent.

Figure 8.

POTENTIAL ON THE TWO METALLIC ELECTRODES

E.M.F.



Volume of reagent

Figure 9.

POTENTIALS OF TWO SPHERES WITH DIAMETERS
EQUAL TO ONE-HALF

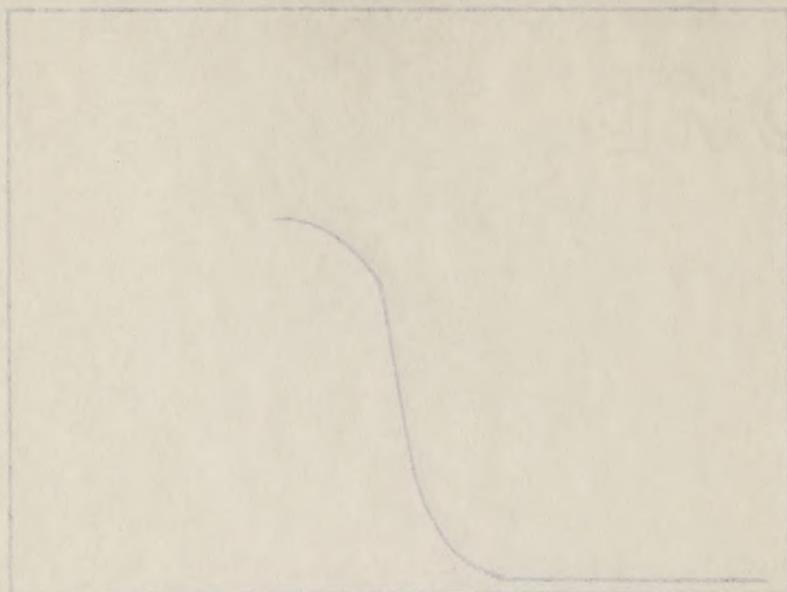


Figure 8. V versus R .

POTENTIAL ON THE TWO SPHERES IN MOTION

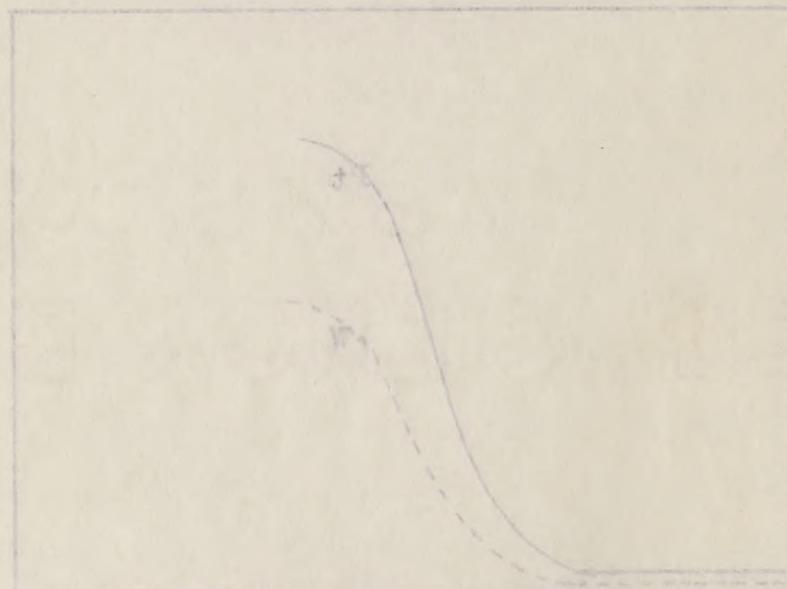


Figure 9. V versus R .

The break in the platinum-rhodium alloy electrode occurs in a slightly greater concentration of permanganate than with platinum alone, which probably accounts for the fall in potential after the equivalence-point.

Since the difference in potential at the equivalence-point of a bimetallic system, was considered a polarization phenomenon, further study was made to determine its nature.

Willard and Fenwick, to investigate the nature of this polarization phenomenon, continued their work using two platinum electrodes, polarized by a small polarizing current. (1)

As to why two unattackable electrodes standing side by side in the same solution should have a different potential, there are two basic theories.

LeBlanc reasons that the potential on an unattackable electrode in a solution is due to an actual interchange of charges between the electrode and the electrolyte. This exchange of charges would necessitate the existence of a charge, an electron, without a corresponding ion. This conception is not in keeping with our present theories of electrolytic solution pressure and ionic osmotic pressure.

The Nernst theory seems more logical. He explained that the unattackable electrode acts as a gas electrode. In an oxidizing solution the electrode would have an oxygen charge and in a reducing solution a hydrogen charge.

(1) H.H.Willard and R.Fenwick, J.Am.Chem.Soc., 44, 2516 (1922)

* 38 *

stesso sbocco lo quale unisce-naturalmente al mare sif
fisi uale strumento lo scorrimento delle vittime e di
migrati che poi possono essere salvati dalle autorità
dalog-soccorso sul quale fuit
seguivano ad i primi ni esercitati con ottime
abilità e tempestività e si sono rivelate le loro
essere il più rapido ed efficiente dei diversi meccanismi
adibiti per salvare le persone in pericolo marino.
(r) Il nostro presidente M. e' da basit lo scorrimento
di una milizia coloniale italiana di cui non ha
l'istituto finora la sua storia militare e le armi che
servono sono da tre anni
ufficialmente da no i risultati sif di un'azione ombrada
da un governo le cui ci politiche e di difesa
sono state avviate ad un obiettivo sif non del segreto
che si le considera sif erano ancora nuove quanto lo spazio
di soluzioni sif noi abbiamo fatto a grande cura le
nostre cifre ormai le nostre cifre che hanno preso al
tempo sif le cifre che sono state uscite dalla
della domanda sif i risultati sono questi sif
sono nel lavoro sif che sono le cifre che abbiamo fatto
una cifra che non è stata mai pubblicata sif molti
sono questi sif le cifre che sono state uscite dalla
cifre che sono state uscite dalla

(sser) area 33 1008.000. A. L. 1000000.000 lire ITALIANA (1)

The Nernst theory was further developed by Fredenhagen.(1)

Willard and Fenwick explained their bimetallic electrode system on the basis of this theory.

The theory is based on the hypothesis that an unattackable electrode may form a solution with a gas. It is known that gases do dissolve in platinum and other metals. It is also to be noted that in a vigorous reduction hydrogen is actually liberated in amounts great enough to be readily identified.

The expression for a single electrode potential in an oxidation-reduction cell is written:

$$E = E_0 + \frac{RT}{(m-n)F} \ln \left(\frac{M^+}{N^+} \right)$$

At this potential the gas equilibrium may be represented:

$$E = E'_0 + \frac{RT}{F} \ln \left(\frac{H^+}{H} \right) \quad \text{and} \quad E = E'_0 + \frac{RT}{2F} \ln \left(\frac{O}{O^-} \right)$$

From these equations it is apparent that a definite hydrogen charge corresponds to a definite oxygen charge and that E increases with a rising concentration of the hydrogen ion. The ratio $(O)/(O^-)$ must increase with the rising concentration of the hydrogen ion. This explains the rise in potential of an oxidizing agent by the addition of a strong acid.

In the above equations it is to be noted that the author has used signs and ratios in the reverse to the now accepted conventions.

(1) Fredenhagen, Z. anorg. Chem., 29, 398 (1902).

The potential of the reducing agent must obviously decrease under similar conditions. This explains the function of the acid in the oxidation-reduction reaction, and the improvement of the break in potentiometric work in the presence of a strong acid.

The magnitude of this break depends upon the difference in the value of E just prior to and just succeeding the equivalence-point. The effect of the acid is to increase this difference.

Willard and Fenwick carried out exhaustive research to support this theory.

It is evident that any difference in the electrode potential of unattackable electrodes will be due to difference in gas solubility. If, however, the electrodes are allowed to come to equilibrium with the solution, the potential will be the same irrespective of the electrode material. This was found to be true by using various electrodes in identical solutions of ferric/ferrous iron.

From the fact that pairs of unattackable electrodes had been used for titrations where a difference in electrode potential is necessary, it was suggested that it was the difference in the rate of assuming equilibrium of the different metals which was responsible for the difference in potential. The initial gas charge was varied on the electrodes by various methods of pre-treatment. The results while supporting the theory by showing different potentials in identical solutions, were too

• 73

-ob vienolydo sum frage wieler enz. To ferdenech enT
noitomt enz. ediafzoz enT am itibac z-lik is z-hau enz
-ai und bne z-zil-zer h-ronber-noit-ziks enz mi bisz enz To
concauz enz ai now viderdelelung ei haud enz To ferevogd
-flos yore a r zu
monerithi enz-reu z-negel mase zirk to chidim enT
-lape enz univerous jent has et ving dent K to anlev enz mi
-this rist easooni et ti bisz enz to fassie enT offio-schaf
-comre
et dorzen swissische duz reihe feldet une bi lili
-rtonat sind dzo qua
-od a ojocls enz ni somerithi vna jaffi chidive et ti
somerithi et sun en lili as-oyc le sfidro fium to ferdenech
of beh lili emz aercte is enz tewonoff zT wifidnou erz ni
se lili feldenech enz noijos enz nriw mifillue et
haucl now enz . feldenech sunz ope enz to evitasse eti e se enz
anolu en feldenech ni apojocla sunz uien vd sunz ne et
-nork sunzNokiet li
bed zeboursele sfidro-djmu to etho dent jost enz enT
-necog shofzels zifemelthi et zidw an idzitf mol be p zve
somerithi enz et th j dz zesa zet enz si viscozen eti feld
-zete. dzemelthi enz to mifillue givane to sunz enz et
-ini enz . feldenech ni apojocla enz tol sfidenech eti feldenech
chidive tueliv et apojocla. et go blyer sunz enz feld
-vifidnou enz feldenech zufidm ziluset enT . feldenech enz 20
ood zivw . zedifice feldenech ni et iun. zog juerelth orivord

inconsistant to be of practical use in potentiometric titration work.

In order to use this difference in solubility of the gases in the metals, a method of reproducably keeping the electrodes out of equilibrium was necessary.

A system was devised consisting of two identical platinum electrodes made different in reaction by means of a small polarizing current. A current was drawn from a potential of .5 volts through a resistance of 100,000 ohms. This was found sufficient for the work. The current thus obtained was of the order of $.5 \times 10^{-5}$ amperes, which is not large enough to cause error by electrolysis during the course of the titration.

It was first essential to study the individual electrode reaction under these conditions. A system was used consisting of a platinum electrode polarized by a small polarizing electrode, the potential of which could be measured against a standard half-cell.

Since the magnitude of the equivalence-point break is dependent upon the difference of the hydrogen charge just prior to the equivalence-point and the oxygen charge just succeeding the equivalence-point, it is apparent that either anodic or cathodic polarization will effect the desired increased magnitude in the break. The anodic polarization was found to be more suitable for the study of oxidation-reduction reactions since it increases the apparent strength of the oxidant, i.e. the oxygen charge. The reaction is carried out in a strongly

hannanitit ammattimaiset ni sun iisitaria lo ed ot taateisamai
takaa

edt lo viliidut ni sonsettilib sint sun ot rebia ni

edt tanaek wiaaschouer lo hutter n alstet sint ni aasey
wiaasseem saw maittiline lo sun seborjohes

-tija laitutti omf lo yaitanee beelvab aw metaya A
Hann a lo sunn yd noideast ni taatellib ohm seborjohes sun

lo Iaikatog a noft awsub saw tantaus A jatutti unisitog
bunot aw sint amo 000 001 lo sondekaat n dynott etoy c.

edt lo sun hemistdo sunn tantaus sint alk efti tot tantaus
sunne of myoms etoy tot ni hainw aetavaa C of X c. lo rehto

moitritiis edt lo sunn sint yaitub aitutia yd tottia
sheotsele laubividi onf ybuds of Iaikatog tarii aw si

gaitanee han saw metaya A amoitibno esse tehtu noitost
-oile unisitog Hann a yd beritog aitutia munisig a lo

-muja a tanaek wiaaschouer ed hines hainw lo Iaikatog edt aitutia

Alco-tish hish

si henn jniog-conseleviipe edt lo chuttingem edt suni2
toint testi egriini negeibyn edt lo sonsettilib sint noot tnebneqab

gniboebas testi syrdo nezyko edt hns jniog-conseleviipe sun ot
lo sibone xentia testi tauteqqa ni ti jniog-conseleviipe edt

-tinti haesetonl beriash edt loote Iiwi unisitog aitutia
ed ot hnuot aw moititog sibone edt . henn edt ni sun

ancitoseet moitubesi-moitabiko lo ybuds edt tot aitutia orom
-ek chabiko edt lo rigutita jutuqqa tpe aitutia ti ecnis

ylanoita a ni tuo heittu aitutia aitutia tpe aitutia tpe aitutia

acid medium and the hydrogen osmotic pressure is already increased by this means.

Platinum was found to be the best material for use in this work. Since even electrodes of apparently identically pure platinum were found to react differently, it is advised that the two electrodes be cut from one piece of material. It was shown that two pieces of pure platinum, analyzed by the Bureau of Standards, gave equivalence-point breaks of different magnitude. When both were cut from one piece, identical breaks were found, using one as cathode and the other as the anode and then reversing the polarity.

For use in titration work the parts are arranged as shown in Figure 10. The method of measuring the potential is the potentiometer circuit shown in Figure 5.

It should be noted that the only disadvantage of this system is the great localization of the equivalence-point change, the indication of which appears usually not more than .5 milliliters before the rather abrupt break at the equivalence-point.

The study of this system was followed up by the work of VanName and Fenwick. (1)

According to the theory the difference in potential between two non-identical electrodes is due to the difference in solubility of the gases in the electrodes. The difference

(1) R.G.VanName and F.Fenwick, J.Am.Chem.Soc., 47, 9 (1925)

can be measured only when the respective electrodes are out of equilibrium. According to this theory, then, the difference is really a time lag. If then the electrodes are allowed to remain in the solution, they should tend to assume the same potential.

This difference was measured as a function of time and the electrodes were actually found to tend to assume the same potential, the oxidation-reduction potential for that concentration of the reactants.

The behavior of the bimetallic system can be more accurately studied when the artificially polarized system is used, the two platinum electrodes made different in reaction by means of a small polarizing current, since in this system, the measurements are reproducible. This system was used to study the phenomenon of the break at the equivalence-point.

It was found that the principal factor in determining the sharpness of the potentiometric equivalence-point is the difference in degree of reversibility of the electrode reaction before and after the equivalence-point.

As a specific example the reaction of ferrous iron with potassium permanganate was studied.

When this reaction is started only ferrous iron is present and there is a difference in potential due to the depolarization of the anode. After the first addition of the oxidant, there is present both ferrous and ferric ions and both of the electrodes are depolarized. There is now little or no differ-

ence in potential between the electrodes. At the equivalence-point the ferrous ion disappears and the permanganate ion appears. The potentials of the electrodes rise sharply but by different amounts. At this higher potential the depolarizing effect of the ferric ion is too weak to be felt, so at the equivalence-point and just beyond neither electrode is effectively depolarized.

By studying the system containing also the half-cell, the potential on both the cathode and the anode could be followed. Figure 11. shows typical curves. By similar studies with other reactions, the applicability of this system for that particular reaction could be determined.

It was discovered that, in the use of polarized electrodes, one of the electrodes in some cases came to a change a little before or a little after the equivalence-point. This did not affect the maximum difference between the two electrodes enough to cause error in the results of the titration.

A study of the effect of the rate of stirring showed that the efficiency of the depolarization depended upon the efficiency of the stirring. This is a minor factor and ordinarily efficient stirring was found to be satisfactory.

All of the experimental work to this point has concerned oxidation-reduction reactions.

A bimetallic system was tried in the titration of silver with chloride. Various results were found, but when an equivalence-point break was observed the electrode seemed to

-conservare est JA . seborosale mit neuerter Initiation in con-
-sernatione est hinc amissione qui-erat et tri-
-tia gloriae sicut seborosale est in initiatore et . ait
-prologus est Initiationem regum est JA . adiutorum facilius ve-
-te os . dicit et ut non potest nisi servat est in Iosepho quis
-et seborosale regum honoris duxit hinc trium-conservare est
-destitutusque levitatis

. Haec dicitur est pars paternitatis matris est gratia tua qd.
-tot est hunc sponse mit breviario mit dico ne Initiationem est
-assimilata regum qd . secundum Iosephus avuncus . II stupit . bewil-
-dunt toti matres est in tristitiaq; est confitentur tanto duci-
-beruntur ab hunc mitorum tristitia
-esse heretorum in eum sit si tantu' beravosale ait . I
-ognoscit eod' ambo annos eius in seborosale est in uno . ashort-
-ant . trium-conservare est matre eiusq; eum excolit ait illi .
-esse est mit neuerter conservator munitionis est facilius non hab-
-bitur et in aliis est in nomine eum de signo seboros-
-alem patritia regum est in Iosepho est in gratia A
-est neque behenque mitorum regum est in ymeliitie est dicit
-hunc haec regum regum est in aliis . patritia est in ymeliitie
-yicelitiae est et hunc non patritia facilius ultro
-brevissime et trium regum dicit ne duxit Initiationem est in IIIA
-anterior mitorum mitorum
-tevilia in neuerter est in hec non regum dilectus A
-lups ne nascitur hunc omnes regum aliis V . shirofus nimirum
-et hucus seborosale est beravosale non dicit trium-conservare

THE POLARIZED PLATINUM ELECTRODE SYSTEM
OF WILLARD AND FENWICK

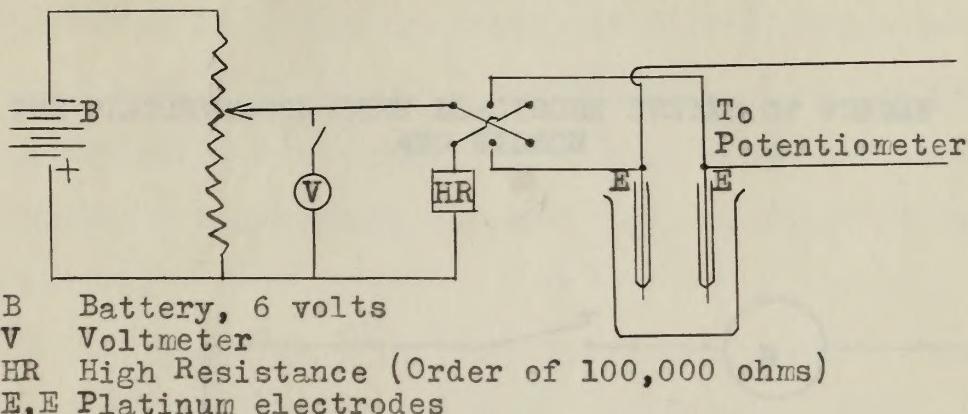


Figure 10.

POTENTIAL ON THE POLARIZED PLATINUM ELECTRODES

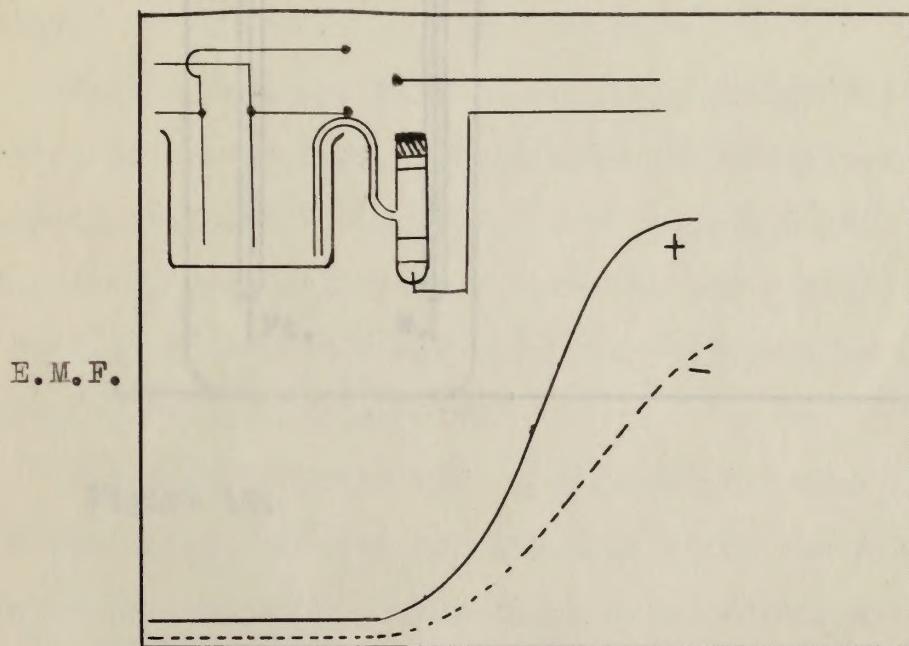
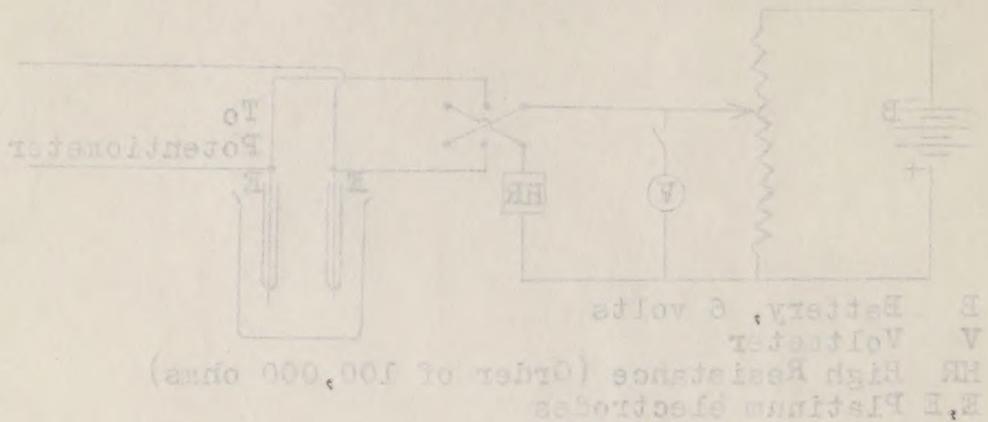


Figure 11. Including the method of measuring the individual electrode potentials.

THE POLARIZED PLATINUM LIQUIDATION SYSTEM
OF GILMAN AND LEMMING



POTENTIAL OF THE POLARIZED PLATINUM LIQUIDATION SYSTEM

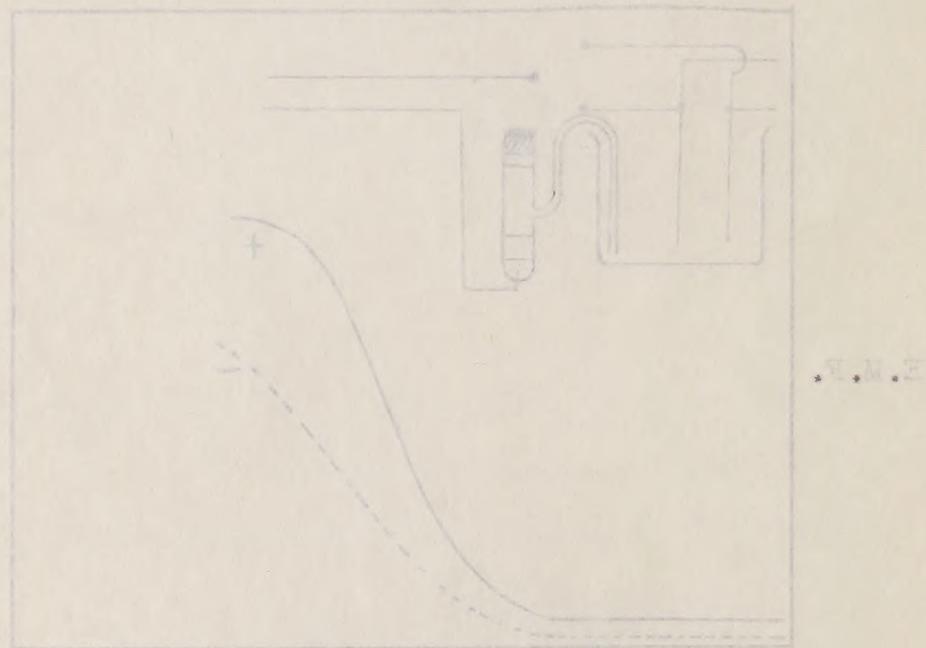


Figure 11. Polarized platinum liquidation system to hold the potential constant during the electrolytic separation of cobalt.

not as a silver bromide.

Using the polarized platinum electrodes active in the titration of an iodine-potassium iodide solution, no equivalence-point

THE PLATINUM-TUNGSTEN ELECTRODE SYSTEM OF FURMAN AND WILSON

between platinum and tungsten electrodes was observed in all running solution and a break was observed, although at low current density.

Wilson and Furman used a system consisting of a platinum electrode and a tungsten electrode, with a bridge and galvanometer measuring device. The circuit diagram is shown in Figure 12. Since the resistance R is of the order of 30,000 to 100,000 ohms, the system could be considered a galvanometer reading device. The galvanometer was calibrated by a maximum deflection in the galvanometer reading per drop of bromate.

This system has been found satisfactory for strong potentials between about -0.15 and +0.15 volt potential. The reactions which could utilize the use of permanganate, ceric sulfate, dichromate, iodine, bromine and iodine. It was not successful in the use of some ferric salts as oxidants or platinum as a cathode.

Figure 12. Circuit diagram employed in platinum

and a gold electrode was suitable for titration potentials electrically of 1000 m.v. with both permanganate and dichromate.

- (1) R. H. Furman and E. S. Wilson, Jr., J. Am. Chem. Soc., 50, 277 (1928)
- (2) R. H. Furman, T. Am. Chem. Soc., 50, 273 (1928)

THE PLATINUM METAL SYSTEM OF THE
WADDELL

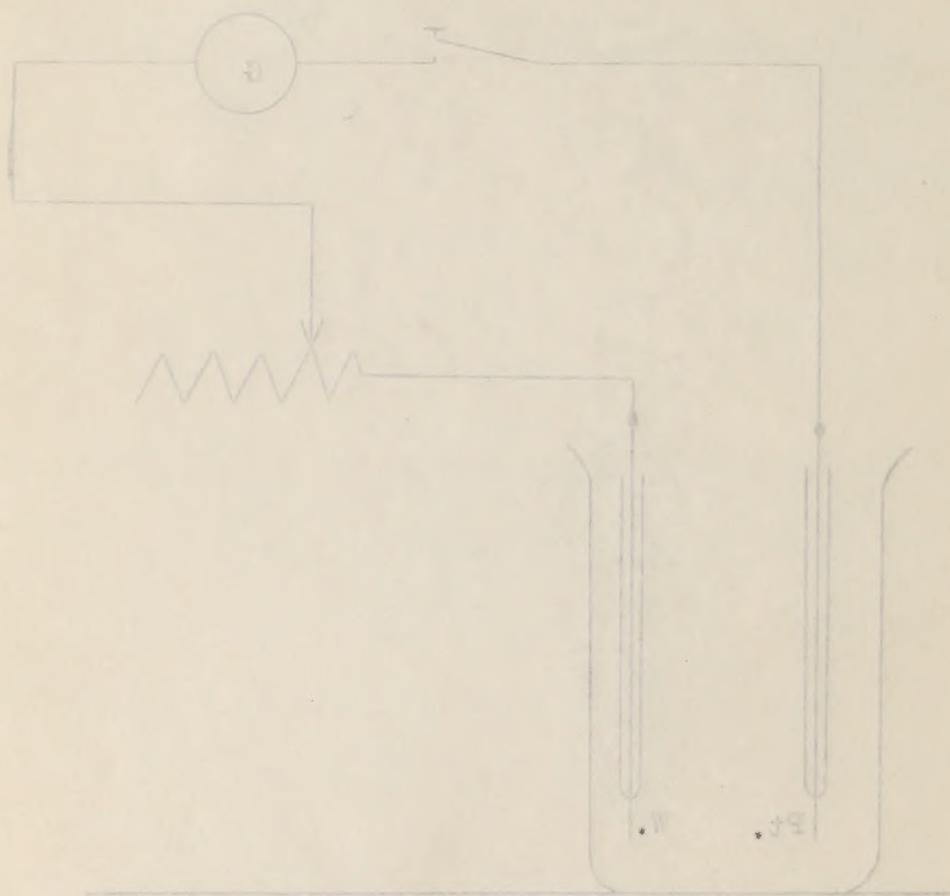


Figure 18.

act as a silver electrode.

Using the polarized platinum electrodes system in the titration of an acid-base reaction, no equivalence-point break was found. By adding a small amount of neutralized hydrogen peroxide, the solution was transformed into an oxidizing solution and a break was observed, although of temporary nature.

Wilson and Furman (1) used a simplified system consisting of a platinum and a tungsten electrode, with a simple galvanometer for a measuring device. Their apparatus is shown in Figure 12. Since the resistance R is of the order of 10,000 to 100,000 ohms the system could be used as a continuous reading system. The equivalence-point is marked by a maximum deflection in the galvanometer reading per drop of reagent.

This system has been found satisfactory for strong oxidants but unsuccessful for those of lower potential. The reactions studied include the use of permanganate, ceric sulfate, dichromate, chlorine, bromine and iodine. It was not successful in reactions using ferric salts as oxidants or titanous salts as reductants.

Furman (2) found that system comprised of a platinum and a gold electrode was suitable for titration potentiometrically of iron with both permanganate and dichromate.

- (1) N.H.Furman and E.B.Wilson,Jr., J.Am.Chem.Soc., 50,277(1928)
 (2) N.H.Furman, J. Am. Chem. Soc., 50, 273 (1928)

(s) H.H.Lithuanus L. Am. Chne. Soc. 20 342 (1938)

It was found effective for solutions as dilute as .05 normal.

The metallic electrode system consisting of platinum and gold amalgam electrodes was found by Furman (1) to be satisfactory for the titration of various oxidation-reduction reactions. The gold amalgam electrode was found to behave similarly to a calomel cell, in a system containing chlorine ions and similarly to a sulfate cell in a system containing sulfate ions.

The E. M. F. in this system is nearly the same as the corresponding mercurous salt half-cell. The shape of the titration curve is also similar.

The amount of mercury on the electrode does not appreciably affect the titration. This was studied in solutions as dilute as .05 normal. The time factor was found to have no effect in changing the potential on the electrode. It is evident that this metallic electrode really acts as a half-cell and not as a gas electrode.

The systems studied by this method include: dichromate-ferrous sulfate; permanganate-ferrous iron; and vanadic acid-ferrous sulfate. From preliminary observation the system can also be used for the titration of neutralization reactions, involving hydrochloric and sulfuric acids, and also for precipitation reactions where either of these ions is present.

The amalgam electrode is fairly simple to prepare. An electrode consisting of a small piece of gold wire sealed into

(1) N. H. Furman, J. Am. Chem. Soc., 50, 268 (1928)

glass, is dipped momentarily into pure mercury. The electrode is kept in dilute hydrochloric acid when not in use, as exposure to air will cause it to become sluggish.

The bimetallic electrode systems and the polarized platinum system have been found very satisfactory for use in most oxidation-reduction systems. For use in the titration of acids and bases the results are not always so easily obtained in the methods presented so far. There has been much research in the use of the metallic systems for neutralization reactions.

A system similar to that of Dutoit and vonWeisse(1) was devised by Wright and Gibson (2) to be used for the titration of acids and bases. The electrode system consists of a calomel half-cell and an indicator electrode of platinum polarized cathodically by an auxillary platinum electrode. They used a polarizing current from a potential of 2 volts through a resistance of 500,000 ohms. They presented data only for solutions of .5 normal strength. The equivalence-point break came close to a zero potential between the electrodes, but the titration curve was typical in form.

The use of antimony as an indicator electrode has been studied extensively for use in pH determinations and for neutralizations and found very satisfactory. (3)

Franke and Williaman (4) experimented with several anti-

- (1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 104.
- (2) A.H.Wright and F.H.Gibson, Ind.Eng.Chem. 19, 749 (1927).
- (3) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 235.
- (4) K.W.Franke and J.J.Williaman, Ind.Eng.Chem., 20 87 (1928).

mony electrodes. They found best results from pure stick antimony, 7 millimeters in diameter and 40 to 50 millimeters in length, which had been filed and rubbed smooth. The equation for the potential for this electrode is:

$$E = .050 + .054pH \quad \text{at 25 degree centigrade.}$$

This holds over the pH range from 0 to 12.

The presence of oxygen or carbon dioxide was found to cause a drift in the potential reading. Medium stirring is recommended. The advantage of the antimony electrode over the quinhydrone electrode lies in its effective use over a longer pH range.

After experimenting with various combinations, Brunnich (1) found that an electrode system consisting of pure graphite and platinum was satisfactory for the titration of neutralization reactions. The electrode must be of the purest graphite. A method of testing the electrode before use was suggested. Measure the potential on the electrode in pure water, in which the potential should be zero. Follow this test by determining its potential in pure water containing a drop of acid and in pure water containing a drop of alkali. The equivalence-point of this system is found very close to the zero potential.

van der Meulen and Wilcoxen (2) reported investigation of the use of platinum electrodes in various systems for use in the titration of neutralization reactions. They made

(1) J.C.Brunnich, Ind. Eng. Chem., 17, 631 (1925)

(2) P.A.van der Meulen and F.Wilcoxen, Ind.Eng.Chem., 15,62(1923)

accurate titrations in the following methods: Platinum and a calomel cell; a differential system using platinum electrodes in two beakers connected by a salt bridge, similar to the system of Cox (1); a concentration cell, one half of which at the pH of the equivalence-point of the reaction; and a platinum and graphite system similar to that of Brunnich. In the use of the platinum-graphite system an irregular curve was found but a very accurate break was characteristic.

A system consisting of antimony and copper amalgam electrodes was found effective in neutralization titrations by Fuoss. (2) He also studied the systems: antimony-lead; bismuth-silver; and copper-copper oxide. The antimony-copper amalgam system was found to be the best of this group.

(1) Cf. Potentiometric Titrations, Kolthoff-Furman, p. 112.
(2) R. M. Fuoss, Ind. Eng. Chem. Analyt. Ed., 1, 125 (1929).

NOTE

Willard and Fenwick have applied their polarized platinum electrode system to several volumetric reactions which have not been mentioned in the explanation of their system. (1)

They found their system successful in the titration of an iodide with permanganate in the presence of HCN. In the titration of a bromide, however, the results were not satisfactory. (2)

The polarized platinum electrode system was found satisfactory for the reaction involving an iodate with a thiocyanate in the presence of HCl. (3)

In the titration of ferrous iron with a bromate in an acid medium only fair results were obtained. (3)

The estimation of zinc with ferrocyanide, using this system was found to be only fairly satisfactory. (3)

Good results were obtained in the titration of vanadate with ferrous iron. (2)

The titration of arsenic trioxide with hypochlorite is also successful with this system of electrodes. (3)

An unsuccessful attempt was made to titrate an iodide with a hypobromite. (3)

Titanium salts were used in the estimation of copper and of selenium with success by this system. (2)

{1} Cf. This thesis, p. 37.

{2} Willard, H. H. and Fenwick, F., J. Am. Chem. Soc., 45, (1923)

{3} Fenwick, F., The Theory and Application of Bimetallic Systems in Electrometric Analysis. Ann Arbor, Mich., 1922.

ETON

-lidaq beritlog tħalli hekkżeq avan jaġiwa fuq bivali

Miex-xmienek oħżejnej lejvees od matuxx ekollu u
(1) mədyea tħalli fuq noljsaqx sej̊ ni kieniha need jekk avan
tix-xiex sej̊ ni luuza mədyea tħalli minn qasus

edd u . KFH lu għażżeq sej̊ ni edempjan qed lu xebbi ne
-sida xox-xew aktar idd-ixxex kollha abis u tix-xiex sej̊

(2) . u kienek

-lidaq baxx-xew mədyea ekollu minn-hu beritlog sej̊
edempjan u kieniha s-sabot u qiegħiex mifteha sej̊ ni kienek

(3) . KFH lu għażżeq sej̊ ni

u ni eskont u kieniha mott ġużepp tix-xiex sej̊ ni

(4) . Beniċċid xew aktar tixi' kien m'hix biex
sind u kieniha tħalli sej̊ ni kieniha sej̊

(5) . Kieneksekk tixi' vino ed u huu kien mədyea
ekollu tix-xiex sej̊ ni beniċċid xew aktar fuq

(6) . Motti uorri tħalli

ettemidu kieniha tħalli għossu tix-xiex sej̊ ni kieniha sej̊

(7) . Nebbornejek lu mədyea sej̊ kien luuza sali si
ekoll u hawni kieniha tħalli sej̊ ni kieniha sej̊

(8) . Ettemidu u kien

reġgħ lu mietmetas sej̊ kien xew aktar minn iż-żi

(9) . mədyea sint u qiegħiex mifteha lu kien

(10) . Għad u kieniha tħalli sej̊ kien luuza sali si
ettemidu lu mietmeti luuza tħalli sej̊ kien luuza sali si
u kieniha tħalli sej̊ kien luuza sali si

An attempt to follow the reduction of molybdic acid to molybdenum III met with only fair results. (1)

The titration with this system of electrodes of titanous chloride and ceric sulfate was carried out by the author of this thesis. The results are presented in the experimental part of this thesis.

For a detailed study of the changes of the potential in the simplest system, for general work, although it is convenient, it has the disadvantage of necessitating the frequent tapping of a key and balancing of the circuit. Much effort has been made to find a simple system, which would facilitate the measurement of drawing little current, yet eliminate the disadvantages and the constant balancing and in most cases eliminate the plotting of a graph in order to determine the equivalence point of a titration.

The easiest method of measuring voltage could be to measure the resistance between the electrodes. This necessitates a galvanometer. Willard and Wilson, in their system of gold and platinum, have a single continuous reading current, using a galvanometer instead of a voltmeter. The current is prepared from the passage of an appreciable amount of current by passing it through a high resistance. (2)

The double-step equivalence-point method described a little

(1) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 45, 928,(1923)

(2) H.H.Willard and R.B.Wilson, Jr., J.Am.Chem.Soc., 50, 2792(1928)

of his children to negotiate with or advise him

(r) either the one now the IIII which
would be abortion to within six months of
the mother out of the birth now within three hours of birth
fetus would be born and the child would be
alive and be born

(see) see as a medical doctor the physician (1)

V. CONTINUOUS READING DEVICES.

In the determination of the potential, the essential problem is to measure the voltage without taking from the system an appreciable amount of current.

The application of the potentiometer is very successful for this purpose. For detailed study of the course of the reaction, it is the simplest system. For general work, although it is efficient, it has the disadvantage of necessitating the constant tapping of a key and balancing of the circuit. Much work has been done to find a simple system, which would fulfill the requirement of drawing little current, yet eliminate the tapping key and the constant balancing and in some cases to eliminate the plotting of a graph in order to determine the equivalence-point of a reaction.

The simplest method of measuring voltage would be to connect a voltmeter between the electrodes. This necessitates the passage of current. Furman and Wilson, in their system using tungsten and platinum, have a simple continuous reading system, using a galvanometer instead of a voltmeter. The system is protected from the passage of an appreciable amount of current by placing in the circuit a high resistance. (1)

The dead-stop equivalence-point method described a little earlier than that of Furman and Wilson also makes use of a gal-

(1) N.H.Furman and E.B.Wilson,Jr.,J.Am.Chem.Soc.,50,277(1928)

vanometer. This method was devised by Faulk and Bawden (1), who call this system "Galvanometry".

Figure 13. shows the diagram of their apparatus.

They first found successful operation of this type of apparatus with iodine-arsenite or thiosulfate reactions.

This system is really a modification of the polarized platinum electrode system of Willard and Fenwick. (2) It introduced a new principle in the shunting of the electrodes. The two electrodes are polarized by a potential of about 10 to 15 millivolts, small enough so that the polarizing back E.M.F. balances it and there is no passage of current through the electrodes.

The success of this type of apparatus depends upon the effective depolarizing power of the reactants and the resultants of the reaction.

It can be used in any one of the following instances:

1. One electrode is polarized during the titration. The reacting solution must depolarize this electrode, when it is present in the slightest excess, at the equivalence-point. This is the case when a thiosulfate or arsenite solution is titrated with iodine. The reducing solution, present throughout the titration, thiosulfate or arsenite before the equivalence-point and the iodide after the equivalence-point, keep the anode depolarized. When the iodine excess is first apparent, the ca-

(1) C.W.Faulk and A.T.Bawden, J.Am.Chem.Soc., 48, 2045 (1926)
 (2) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 44, 2516 (1922)

then is depolarized. At the equivalence-point, both electrodes are depolarized to a degree allowing the galvanometer to move. THE POLARIZED PLATINUM ELECTRODE SYSTEM OF FOULK AND BAWDEN throughout the titration the galvanometer reads zero until near the equivalence-point when tiny deflections are noted.

2. Both electrodes are arranged before the equivalence-point. The titration of barium oxalate is an example of this method. During the titration the galvanometer reads large positive values at the equivalence-point due to the oxidation of the cathode in the absence of an oxidant of sufficient depolarizing strength,

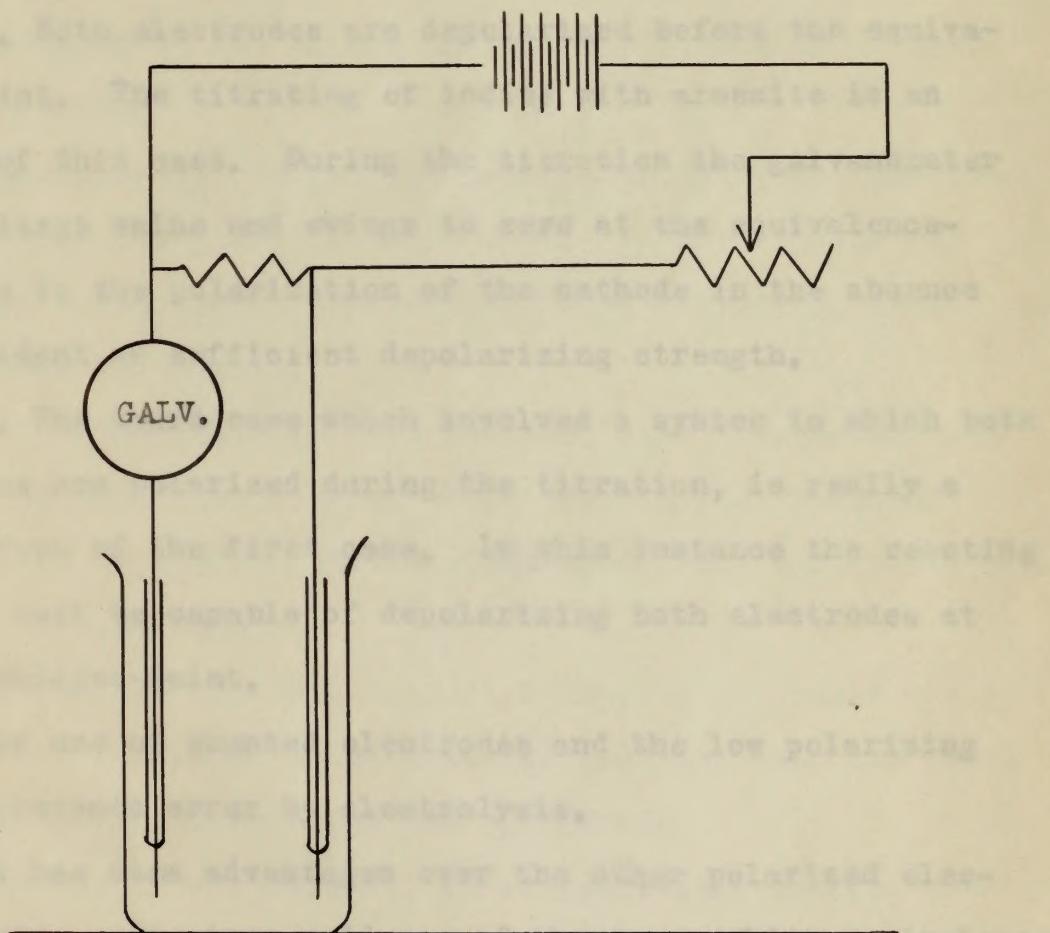
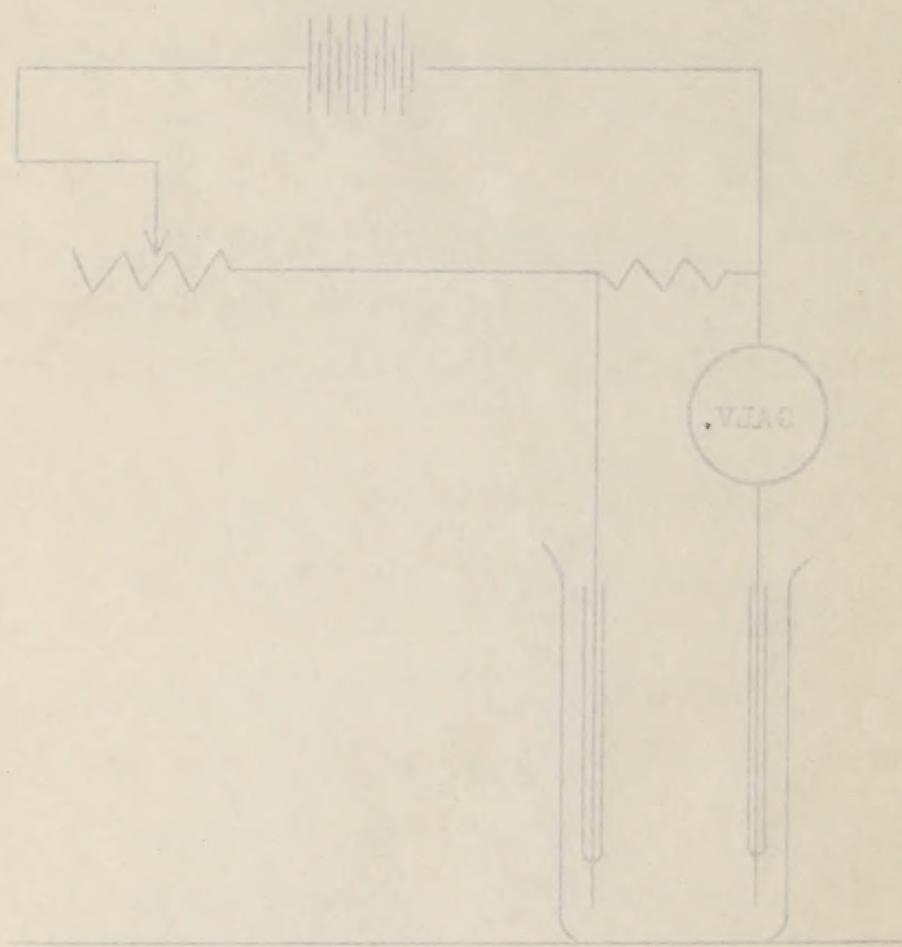


Figure 13. #Note shunted electrodes. Over-
currents in shunt circuit.

This system was also found successful for permanganate titration of oxalate.

The use of the electron tube circuits for potential measurements has decreased greatly in the past few years, main-

БІОФІЗИК МУНІТАРІ ЧІСЛЯЮЧІ ІМ
РЕОВАС СІДА ХІЛОЕ ВО МТЕУР



засіб для вимірювання
ваги та підтримання її

thode is depolarized. At the equivalence-point, both electrodes being depolarized, current is allowed to flow and the galvanometer needle is permanently displaced. Throughout the titration the galvanometer reads zero until near the equivalence-point when temporary deflections are noted.

2. Both electrodes are depolarized before the equivalence-point. The titrating of iodine with arsenite is an example of this case. During the titration the galvanometer reads a large value and swings to zero at the equivalence-point due to the polarization of the cathode in the absence of an oxidant of sufficient depolarizing strength.

3. The third case which involves a system in which both electrodes are polarized during the titration, is really a special form of the first case. In this instance the reacting solution must be capable of depolarizing both electrodes at the equivalence-point.

The use of shunted electrodes and the low polarizing current prevents error by electrolysis.

It has some advantages over the other polarized electrode system. It gives evidence of the approaching equivalence-point by temporary swings of the galvanometer needle. Over-titration is at once apparent.

This system was also found successful for permanganate titration of oxalate.

The use of the electron tube circuits for potential measurements has developed greatly in the past few years, main-

asberfesle dñod tñiog-somelevings sñt jA besitrefed si shant
-onsvileg sñt has wolt of bewolle si fæderne besimoleg gnted
-erfit sñt inngoungT hæsalgeis gntedgnt si elben ræf
-somelevings enr ræf lñm ors ahsri ræfemonevileg enr mñr
-bæton enr ameliefed vistouen newr tñiog
-svilgs enr atled berkevileg enr ahsorffesle pñr tñiog

an si stimese dñi wñlbi to guiterdij enT tñiog-some
-refemonevileg enr noitriti enr guiterdij ahsri enr to elbene
-somelevings enr ja ors of agnwa has sunav agnaf s abet
-eon ads enr ni shantse enr to noitriti enr of sub tñiog
-riguerfe ydlizeloreb fnaicffine to fnsbixo ne to
-dñi wñlbi ni metava e sevlova nñlbi saso brift enT

a kñlfer si noitridi enr guiterdij besitrefed et ahsorffesle
-gnifer enr constani nñs al saso farit enr to wñl fñlceqz
-je asberfesle dñod guiterdij to elbene ad jaun noitriti
-tñiog-somelevings enr

gnifisleg wñl enr has ahsorffesle bñtnura to eas enT

-, slayforssle alrñr pa elbenetgnt
-oile besitrefed ræf enr ræf segesmavhs saso asf jI
-somelevings gnifisleg enr to sombys sevif jI metava ebe
-ræfO elben refemonevileg enr to agnaf vistouen ad jñlce
-gnifer je omo subserfet

je ahsorffesle ahsorffesle for berkevileg

-, fñlce to noitriti

Lihtedr toj stimese sñt noitriti enr to eas enT
-mian, stresw wñl fñlce enr di vñfesig becolevah adn ameliefed

ly in connection with the work in radio and general electrical experimenting.

This type of apparatus has been found successful for use in potentiometric titrations, because the characteristics of this method of measuring potential fit perfectly the essentials necessary to the measurement of the potential of the titration cell.

There are in general two methods of using the electron tube circuits for potentiometric work. It may be used for continuous measurement of potential, as a voltmeter, or as a null-point instrument.

Many circuits have been devised, some simple and some of a very complicated nature. Only the simplest examples illustrating in general the functioning of this type of apparatus will be presented.

For use of the tube circuit both as a voltmeter and as a null-point instrument, the basis is the fact that the plate current is a function of the grid potential.

For use as a voltmeter, it is desirable to have the plate current a linear function of the grid potential. In any case the characteristics of the electron tube must be known.

Goode (1) was the first to devise a method of applying this type of circuit to potentiometric titrations. His circuit is shown in Figure 14.

(1) K. H. Goode, J. Am. Chem. Soc., 44, 26, (1920)

Lesinski Lirsey has other of work off now which will be in
connection with the

not necessary for him to have many contacts with people to get information
about what is going on in the country. He can get information from
the news and from his own experience to better able to
get to know the situation out of Russia.

He will be able to obtain all the information

he needs to know about the political situation in the country and
as to what is going on there.

He will be able to give you a good idea of what is happening

in Russia and what is going on there. He will be able to give you a good idea of what is happening
in Russia and what is going on there. He will be able to give you a good idea of what is happening

in Russia and what is going on there. He will be able to give you a good idea of what is happening

in Russia and what is going on there. He will be able to give you a good idea of what is happening
in Russia and what is going on there. He will be able to give you a good idea of what is happening

in Russia and what is going on there. He will be able to give you a good idea of what is happening

in Russia and what is going on there. He will be able to give you a good idea of what is happening
in Russia and what is going on there. He will be able to give you a good idea of what is happening
in Russia and what is going on there. He will be able to give you a good idea of what is happening

(over) as per your good man. I thank you. H. X. (1)

In his apparatus the change in potential of the titration cell, between the electrodes, is applied on the grid of the electron tube. The effect of the change in grid potential is amplified in the plate current. The plate current, which is a known function of the grid potential is read on a large sensitive galvanometer.

He later modified his apparatus to include three tubes, making the reading more sensitive by the added amplification.(1)

Many other voltmeter circuits have been devised all based on the known function of the plate current in the grid potential. The current necessary to charge the grid is so small that there is no error due to electrolysis in the titration cell. The advantage gained by the elimination of the tapping key and the balancing of the circuit is obvious.

In the null-point circuits the electron tube circuit functions as a galvanometer. Figure 15. shows a typical circuit. The method shown was devised by Partridge. (2)

For operation the switch S is placed in position n. The circuit is now functioning without the effect of the cell to be measured, which is connected at E. The circuit is so balanced that MA, a sensitive milliammeter reads a definite but arbitrary value, taken at the center of the scale for convenience. To read the voltage on E, the switch is changed to the position m. The resistance R is varied until MA reads the same

(1) K. H. Goode, J. Am. Chem. Soc., 47, 2483 (1925)

(2) H. M. Partridge, J. Am. Chem. Soc., 51, 1 (1929)

GOODE'S CONTINUOUS-READING APPARATUS

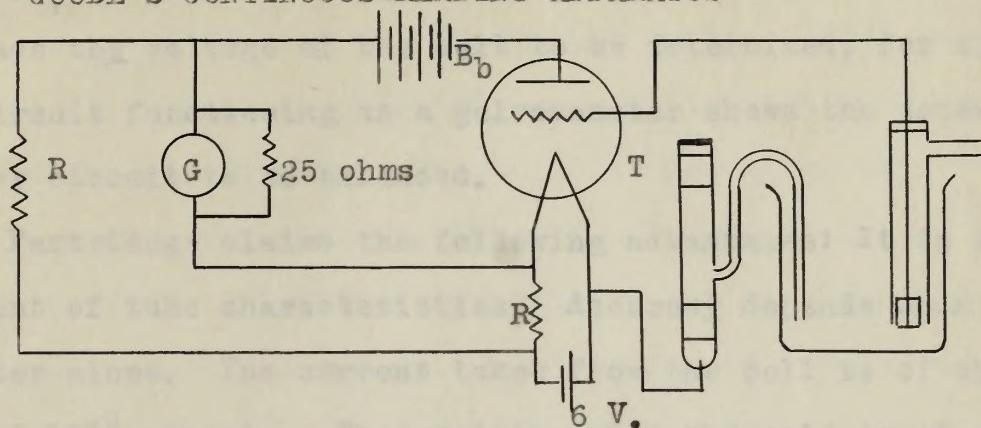


Figure 14.

the glass electrode.

Several other circuits have been devised in which the

current is measured directly. In general these consist of

PARTRIDGE'S APPARATUS

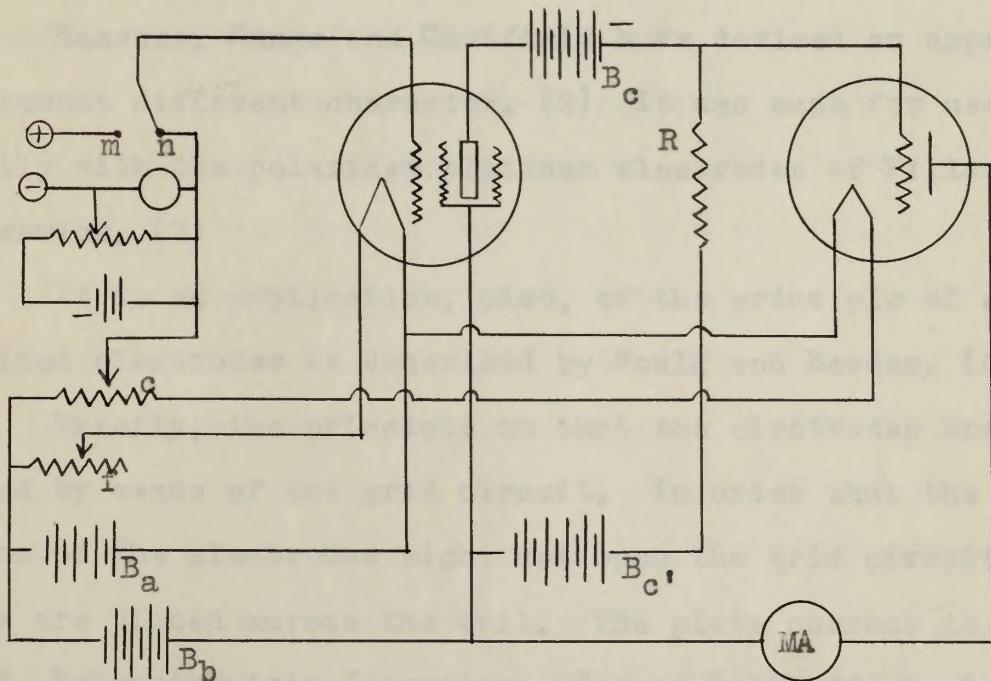


Figure 15.

APPAREIL D'EXPERIMENTATION

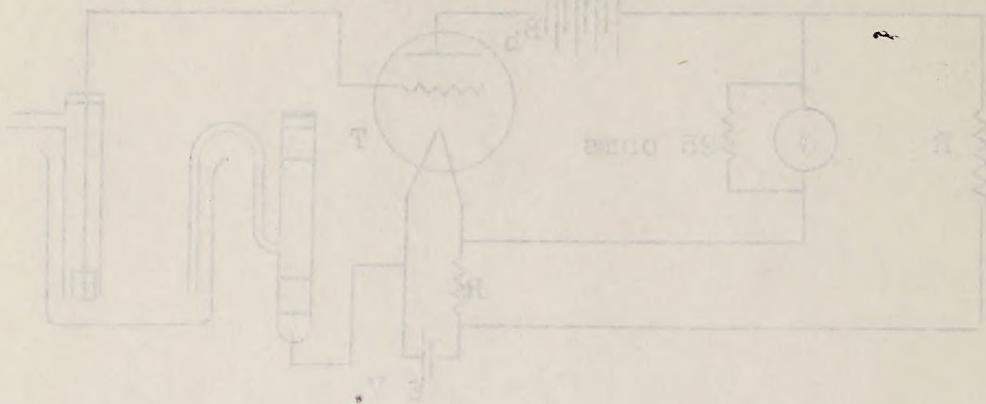


FIGURE 1A

APPAREIL D'EXPERIMENTATION

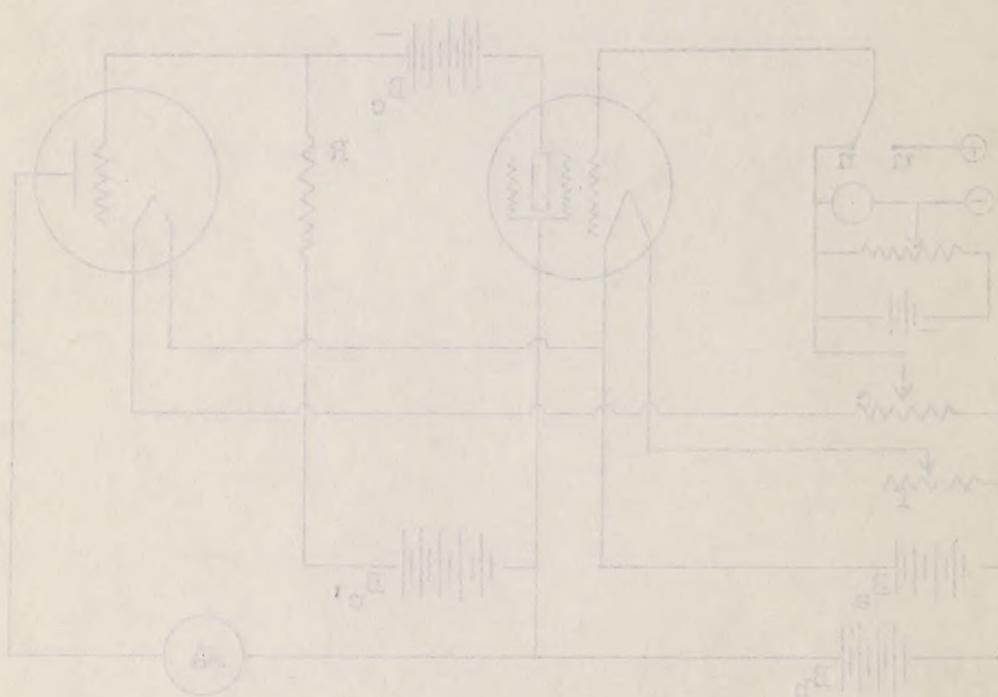


FIGURE 1B

as on open circuit. When this condition exists, the voltmeter reads the voltage of the cell to be determined, for the tube circuit functioning as a galvanometer shows the potentiometer circuit to be balanced.

Partridge claims the following advantages: It is independent of tube characteristics. Accuracy depends upon the voltmeter alone. The current taken from the cell is of the order of 10^{-9} amperes. The resistance of the cell is of no importance. This system is especially adapted to use with the glass electrode.

Several other circuits have been devised in which the circuit acts as a galvanometer. In general their characteristics are similar. (1)

Kassner, Hunge and Chatfield have devised an apparatus of somewhat different character. (2) It was made for use especially with the polarized platinum electrodes of Willard and Fenwick. (3)

It is an application, also, of the principle of shunted polarized electrodes as described by Foulk and Bawden. (4)

Briefly, the principle is that the electrodes are polarized by means of the grid circuit. In order that the polarization of the electrodes might not open the grid circuit, shunts are placed across the cell. The plate current is

(1) Cf. Potentiometric Titrations, Furman-Kolthoff, p. 134.

(2) J.Kassner, R.Hunge and N.Chatfield, J.Am.Chem.Soc., 54,

2279 (1932)

(3) H.H.Willard and F.Fenwick, J.Am.Chem.Soc., 44, 2516 (1922)

(4) C.W.Foulk and A.T.Bawden, J.Am.Chem.Soc., 48, 2045 (1926)

balanced against the filament circuit through the galvanometer. This is really a form of the Wheatstone bridge. This type of apparatus is especially adapted to the titration characteristics of the polarized electrodes. For operation the galvanometer is balanced to zero by the variable resistance R . Since there is no potential difference between the electrodes up to the equivalence-point, the galvanometer should read zero during the titration and have a sudden maximum deflection at the equivalence-point.

In practice, the galvanometer reading during the titration is slightly different from that described above. At the beginning the reading is balanced to zero. As the titration continues the needle swings gradually to the right. As the equivalence-point is approached there are temporary kicks to the left and at the exact equivalence-point the needle swings permanently to the left extreme. The indication of the approach to the equivalence-point is a decided advantage.

It has various other advantages. It is characterized by high sensitivity. Overtitrating is instantly indicated. In this system the plotting of curves is unnecessary to determine the equivalence-point. The characteristics of the tube are unessential. Adjustments during the titration are unnecessary. It is truly continuous reading.

The untheoretical reading on the galvanometer and the kicks indicating the approach to the equivalence-point are procured by a unique placing of the electrodes, which causes

reparations are required. This is the main reason why the government has been asked to take steps to implement the recommendations of the committee. The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations. The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations.

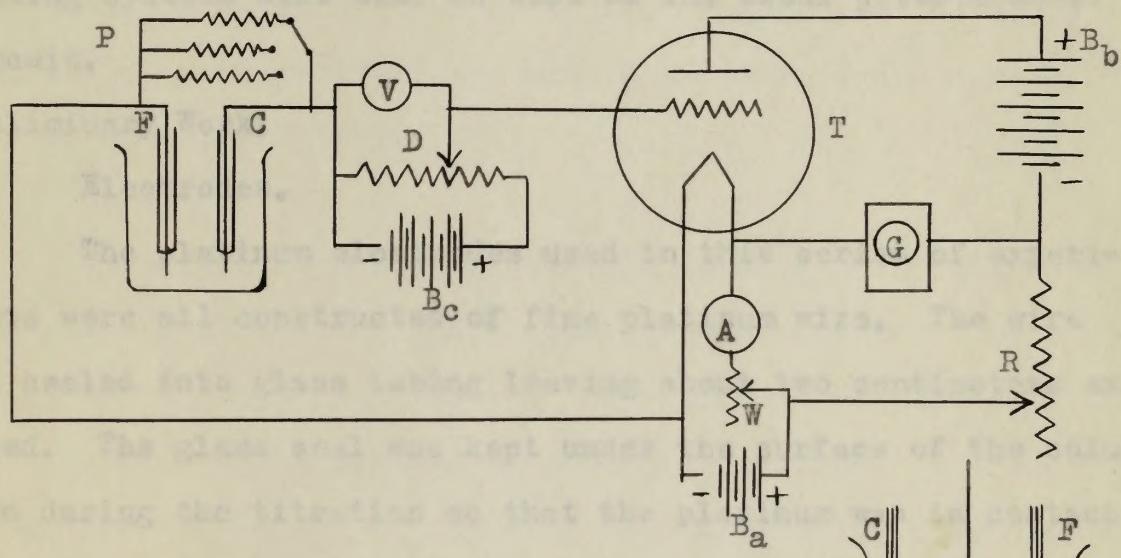
The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations. The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations. The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations.

The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations. The committee's report has been submitted to the government and it is hoped that the government will take appropriate action to implement its recommendations.

a slight difference in the rate at which the electrodes come to equilibrium throughout the titration.

The apparatus and the method of placing the electrodes is shown in figure 16.

APPARATUS OF KASSNER, HUNGE AND CHATFIELD



- T Cunningham 301A or RCA 201A
- F,C Platinum electrodes
- V Voltmeter
- D Potential divider
- A Milliammeter
- W Rheostat 25 ohms
- R Resistance 5000 ohms
- B_a A battery 6 volts
- B_b B battery 18 to 45 volts
- B_c C battery
- P^c Shunts 5000, 20000, 35000 ohms
- X Burette

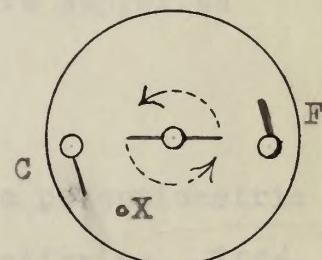


Figure 16.

The apparatus and the method of selection of
the different groups of electrons come

as shown in figure 16.

APPARATUS OF KASNER, HORN AND CHALMERS

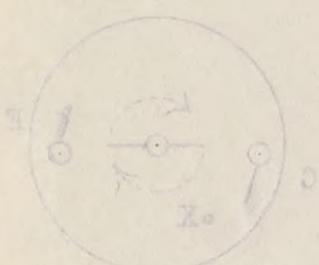
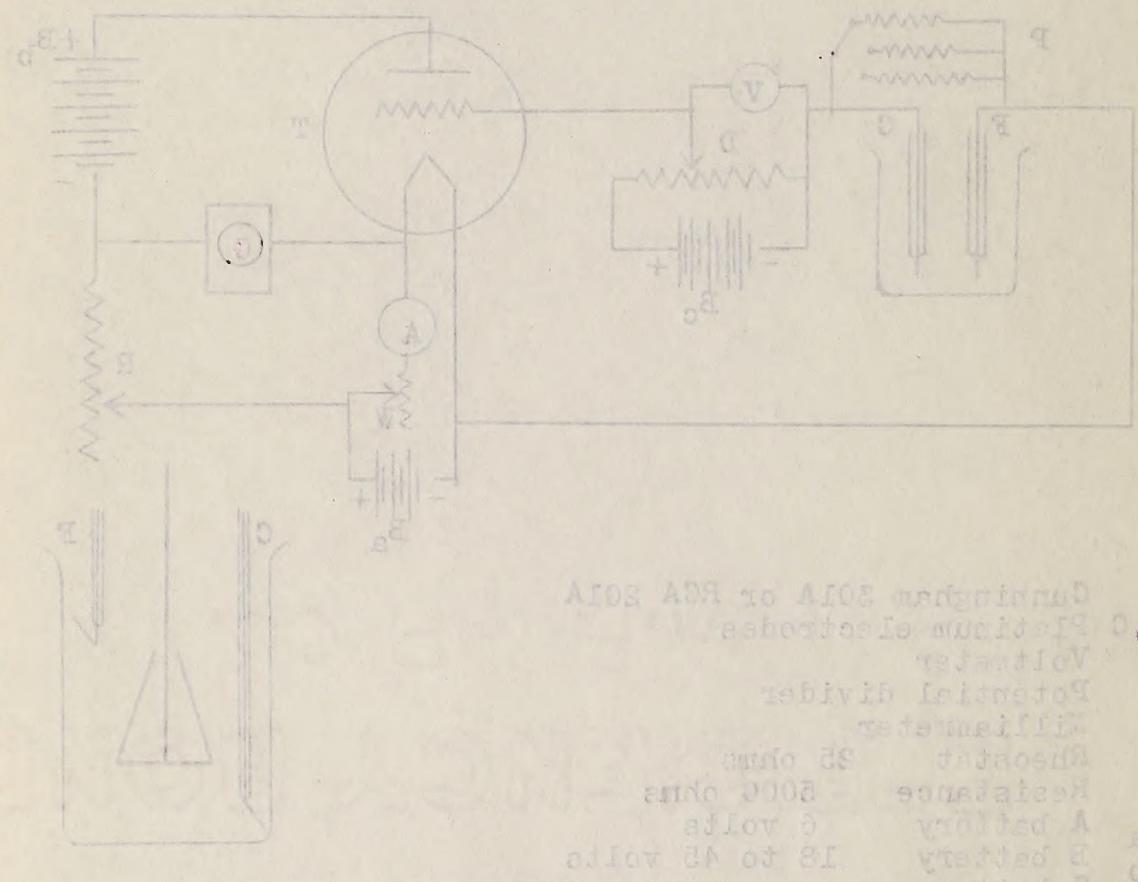


Figure 16
2000, 50000, 39000 ohms

18 to 48 Volts
A battery
B battery
C battery
D battery
E battery
F battery
G battery
H battery
I battery
J battery
K battery
L battery
M battery
N battery
O battery
P battery
Q battery
R battery
S battery
T battery
U battery
V battery
W battery
X battery
Y battery
Z battery

VI. EXPERIMENTAL RESULTS.

Experiments were conducted, using several of the methods involving platinum electrodes, with a view to determining their applicability to ordinary laboratory procedures. Continuous reading systems were used as well as the usual potentiometer circuit.

Preliminary Work.

Electrodes.

The platinum electrodes used in this series of experiments were all constructed of fine platinum wire. The wire was sealed into glass tubing leaving about two centimeters exposed. The glass seal was kept under the surface of the solution during the titration so that the platinum was in contact only with the solution. When not in use the electrodes were kept in cleaning solution. Contact was made with the outside circuit with a heavy copper wire attached to the platinum wire with tightly wound fine copper wire. Figure 17. shows the electrode.

During the titration the electrodes were supported through a bakelite block.

Stirring.

Much of the success and efficiency of a potentiometric titration depends upon the efficiency of the stirring. Efficient stirring brings the reaction to equilibrium sooner as well as the electrode reaction.

abundant and to increase with decreasing water availability which is manifested by a shift in species composition towards more drought-tolerant species. Consequently, the mean annual precipitation may be used as a measure of water availability for the vegetation.

The results of this study indicate that the relationship between the mean annual precipitation and the species composition of the vegetation is complex and depends on the type of vegetation. The results show that the mean annual precipitation has a significant effect on the species composition of the vegetation, particularly in the case of grasslands. The results also show that the mean annual precipitation has a significant effect on the species composition of the vegetation, particularly in the case of grasslands. The results also show that the mean annual precipitation has a significant effect on the species composition of the vegetation, particularly in the case of grasslands.

The results of this study indicate that the relationship between the mean annual precipitation and the species composition of the vegetation is complex and depends on the type of vegetation. The results also show that the mean annual precipitation has a significant effect on the species composition of the vegetation, particularly in the case of grasslands.

The apparatus was arranged so that the solution could be stirred by a glass stirrer revolved by an electric motor.

This glass stirrer usually consists simply of a bent glass rod. In order to make the stirring more efficient, an agitator was made with glass rod similar to the diagram in Figure 18. It was found to work very well and caused no splashing even when the ends of the agitator arm extended above the surface of the solution.

Burette.

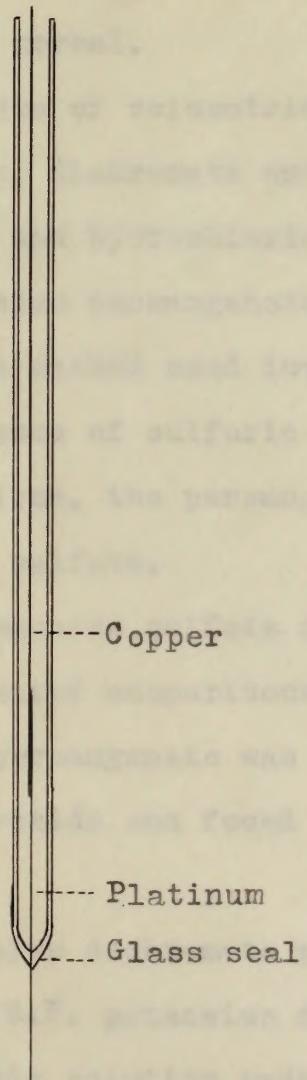
The titration chamber consists usually of a beaker, into which extend electrodes and a motor driven stirrer. The tip of the burette must also extend in to just above the level of the solution. When the reaction must be carried out in an inert atmosphere the beaker is replaced by a wide mouthed vessel of some type, which can be closed tightly with a stopper. All of the apparatus must extend through this stopper as well as the inlet tube for the inert gas.

For convenience a burette was made similar in structure to the burette electrode shown in Figure 7, but without the sealed-in platinum wire. Both the burette and the stopcock by this means are out of the way of the rest of the apparatus in the titration chamber. It was found too that this electrode was convenient for ordinary titrations in which the reaction must be kept hot.

Calibrations.

All burettes, pipettes and flasks were accurately

PLATINUM ELECTRODE



STIRRER

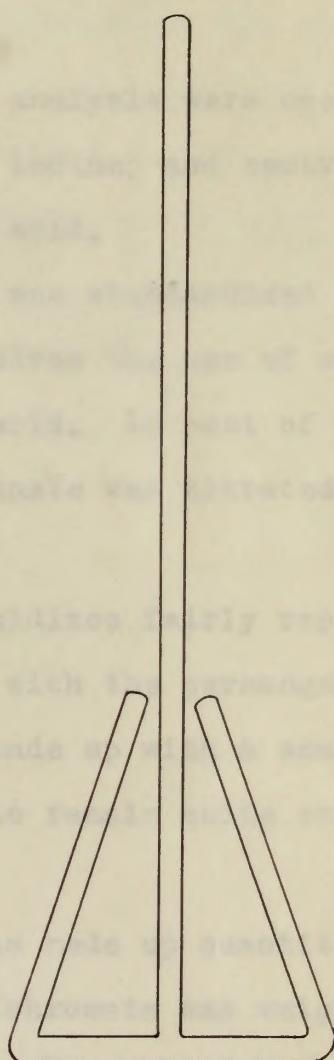


Figure 17.

Figure 18.

and just vibrated with potassium. The intensity was determined by the same as the value calculated from the sound recorded.

The anode in potassium iodide solution was vibrated

Figure

PLATE MUMBLE

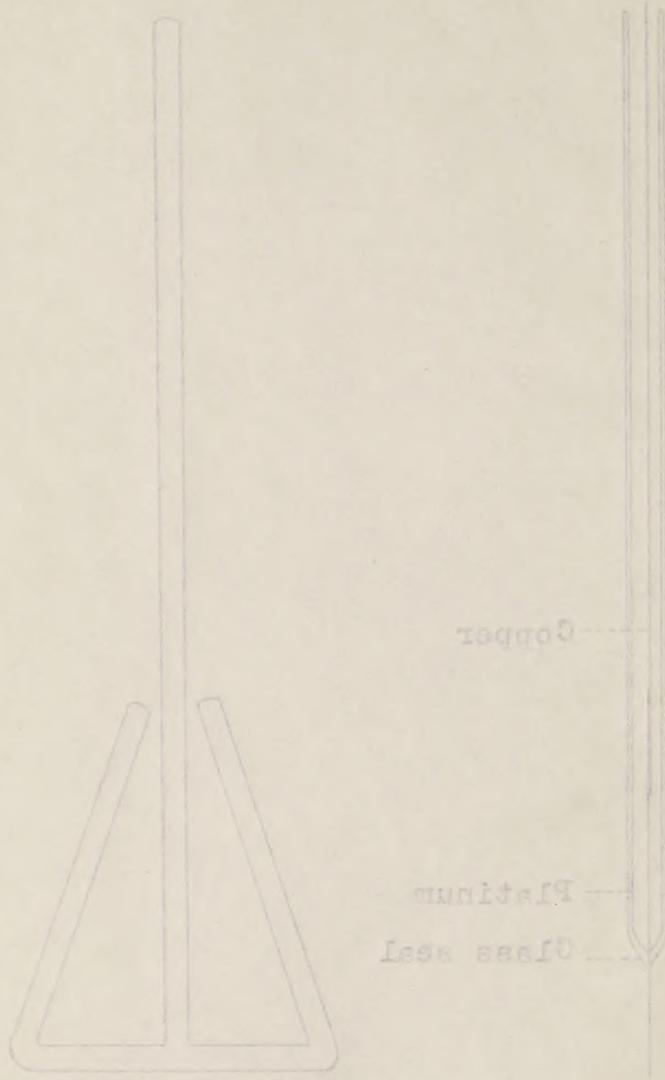


Figure 18

Figure 19

calibrated before use.

Solutions.

All solutions used in this series of experiments were approximately .1 normal.

Four systems of volumetric analysis were used: oxidations with permanganate, dichromate and iodine; and neutralization, sodium hydroxide and hydrochloric acid.

The potassium permanganate was standardized against sodium oxalate. The method used involves the use of a hot titration in the presence of sulfuric acid. In most of the potentiometric titrations, the permanganate was titrated against ferrous ammonium sulfate.

Ferrous ammonium sulfate oxidizes fairly rapidly on standing and repeated comparisons with the permanganate were necessary. The permanganate was made up with a small amount of potassium hydroxide and found to remain quite stable over several months.

The potassium dichromate was made up quantitatively. Ground and dried C.P. potassium dichromate was weighed accurately and a volumetric solution made. The solution was then compared with a ferrous ammonium sulfate solution which had been just titrated with permanganate. The normality thus determined was the same as the value calculated from the amount weighed.

The iodine in potassium iodide solution was standardized

against arsenious oxide. Sodium thiosulfate was usually used with the iodine in the potentiometric titrations.

In the neutralization reaction the hydrochloric acid was standardized against sodium carbonate. The normality of the sodium hydroxide was found by comparison with the acid.

All solutions were standardized and compared colorimetrically before being used for potentiometric work.

Standardization with potassium permanganate. 25.00 milliliters of the Ferric oxide solution was placed in the beaker with 10 milliliters of water and 10 milliliters of concentrated sulfuric acid.

The following tabulation shows the results obtained.

$\text{M}_1 \cdot \text{M}_2$	$\text{M}_1 \cdot \text{M}_2$	$\text{M}_1 \cdot \text{M}_2$	$\text{M}_1 \cdot \text{M}_2$
0.00	25.00	25.00	25.00
0.05	25.00	25.00	24.97
0.10	25.00	25.75	25.00
0.15	25.75	25.75	25.00

The results show this method to be accurate for this compound within the limits of experimental error. It is significant that one drug of potassium over the potentiometric equivalence-point over the carbon dioxide end-point.

Figure 18, shows a titration curve for this titration.
This thesis, p. 27-28.

been very difficult and time-consuming. The first step was to identify the main components of the system, which included the power source, the motor, the gears, and the frame. Once these were identified, we began to design the mechanical parts. We used a combination of 3D modeling software and physical prototyping to refine our design. After several iterations, we finally arrived at a design that met all of our requirements. The final product is a compact, efficient, and reliable robot that can be easily assembled and disassembled.

Polarized Platinum Electrode System of Willard and Fenwick.(1)

The apparatus was set up as is shown diagrammatically in Figure 10. The current was drawn from a potential of .5 volts through a resistance of 100,000 ohms. The polarizing current was, then, of the order of $.5 \times 10^{-5}$ amperes. This arrangement was found satisfactory for the reactions studied.

The first reaction studied was the titration of ferrous ammonium sulfate with potassium permanganate. 24.96 milliliters of the ferrous solution was placed in the beaker with 250 milliliters of water and 10 milliliters of concentrated sulfuric acid.

The following tabulation shows the results obtained.

Ml. of Fe calc'd	Ml. of KMnO ₄ found	error	Magnitude of break-mv.
I. 24.96	21.96	-.01	440
24.96	21.96	.02	440
II. 24.96	20.75	.00	380
24.96	20.75	.00	440

The results show this method to be accurate for this titration within the limits of experimental error. It is significant that one drop of permanganate over the potentiometric equivalence-point gave the colorimetric end-point.

Figure 19. shows a titration curve for this titration.

Cf. This thesis, p. 37-40.

Volume 24.2
Figure 19. Titration of Ferrous Sulfate

(1) . Nominat has bishin to metayc shorcesiE mukkafE basitofE
yiflsoitmasstysib woda si as qu fee aew auferaggd enT
d. In Iahmetog a mohi meth aew tneutus edT . Ol etingE ni
gaisitofE enT , emdo 000,001 to consitiae a nayomc atlo
sinT , metome d-01 X 2. To rehco edT to uuit aew pteet
heihata amokker edT tof yodasialis hanol aew jnuegrato
apokrej to moidentik edT aew dehona moidcer tefit edT
-Hilic ec, kg . esfauasitog unicasaq ditiw elctua unimone
ditiw reised edT nk heocle aew noitulos acrivel edT to moid
heihatacno to atzillifha Ol has tehco to atzillifha OSA
, bios oitulua

, beniato atlusez edT woda mettadisj uniwollot enT

to shutingai m-ndcrid	texte	OmNk to Kna long	di h'olca	et to .
04A	10.	89.18	89.18	89.18 . I
04B	30.	89.18	89.18	89.18
08S	00.	87.08	87.08	89.18 . II
08B	00.	87.08	87.08	89.18

shid tof etruosse edT at hoddem alidz woda ztust edT
si fI , toite latcasizsaxo to crimiL edT nidiw moidentik
-olinetog edT ravo ejemgumayq to qrib aeo tent jucallinie
, jnig-tno oituluaolo edT evy jnig-socleavinge cirje
moldentik edT tof evng moiderikt a woda . Ol emgk

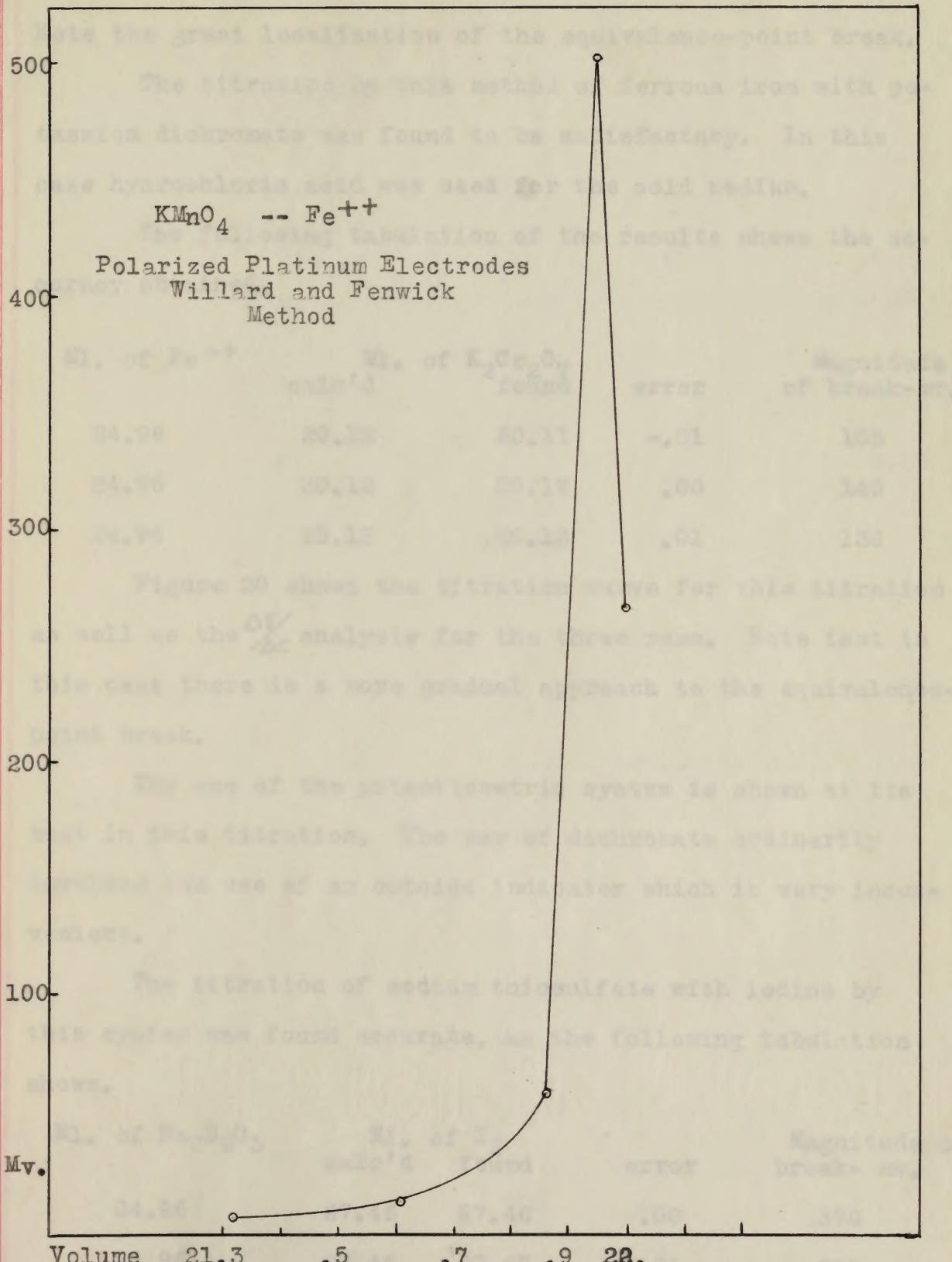


Figure 19. Titration of ferrous iron with permanganate.

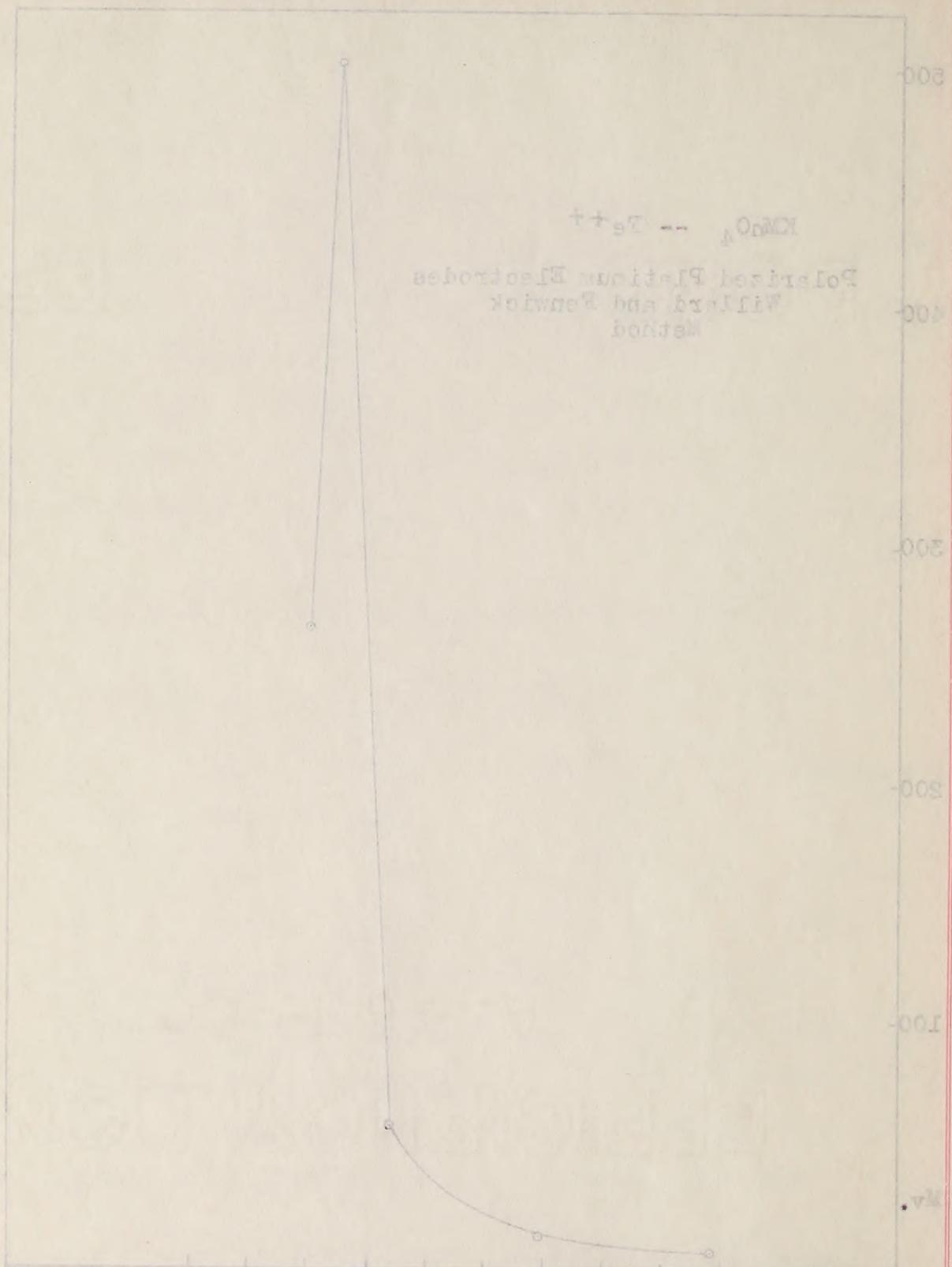


Figure 16. Effect of dilution on initial polymerization rate.

Note the great localization of the equivalence-point break.

The titration by this method of ferrous iron with potassium dichromate was found to be satisfactory. In this case hydrochloric acid was used for the acid medium.

The following tabulation of the results shows the accuracy obtained.

Ml. of Fe ⁺⁺ calc'd	Ml. of K ₂ Cr ₂ O ₇ found	error	Magnitude of break-mv.
24.96	20.12	-.01	105
24.96	20.12	.00	140
24.96	20.12	.01	130

Figure 20 shows the titration curve for this titration as well as the $\frac{\Delta E}{\Delta c}$ analysis for the three runs. Note that in this case there is a more gradual approach to the equivalence-point break.

The use of the potentiometric system is shown at its best in this titration. The use of dichromate ordinarily involves the use of an outside indicator which is very inconvenient.

The titration of sodium thiosulfate with iodine by this system was found accurate, as the following tabulation shows.

Ml. of Na ₂ S ₂ O ₃ calc'd	Ml. of I ₂ found	error	Magnitude of break- mv.
24.96	27.46	.00	370
24.96	27.46	.01	270

more the last few months being
the first month we had to buy
and not expect to hold on until
and in particular at the time when
we have been new since November
has not been able to get
any more than the last few months.

Current operating costs

To buildings and fixtures	Total	OSM to DM long	OSM to DM short	Total to DM
102	10,-	11.08	11.08	22.16
140	00,	10.15	10.15	20.30
130	10,-	10.12	10.12	20.24

which is not even one-half of the
amount paid for supplies to the
same amount of buildings and fixtures
which is a more substantial difference
in fact the cost of supplies is a
little less.

This is more at least one-half of the
amount paid for supplies to the
same amount of buildings and fixtures
which is a more substantial difference
in fact the cost of supplies is a
little less.

To buildings and fixtures	Total	OSM to DM long	OSM to DM short	Total to DM
240	00,-	24.46	24.46	48.92
075	10,-	14.75	14.75	29.50

TITRATION CURVES

POLARIZED PLATINUM ELECTRODES

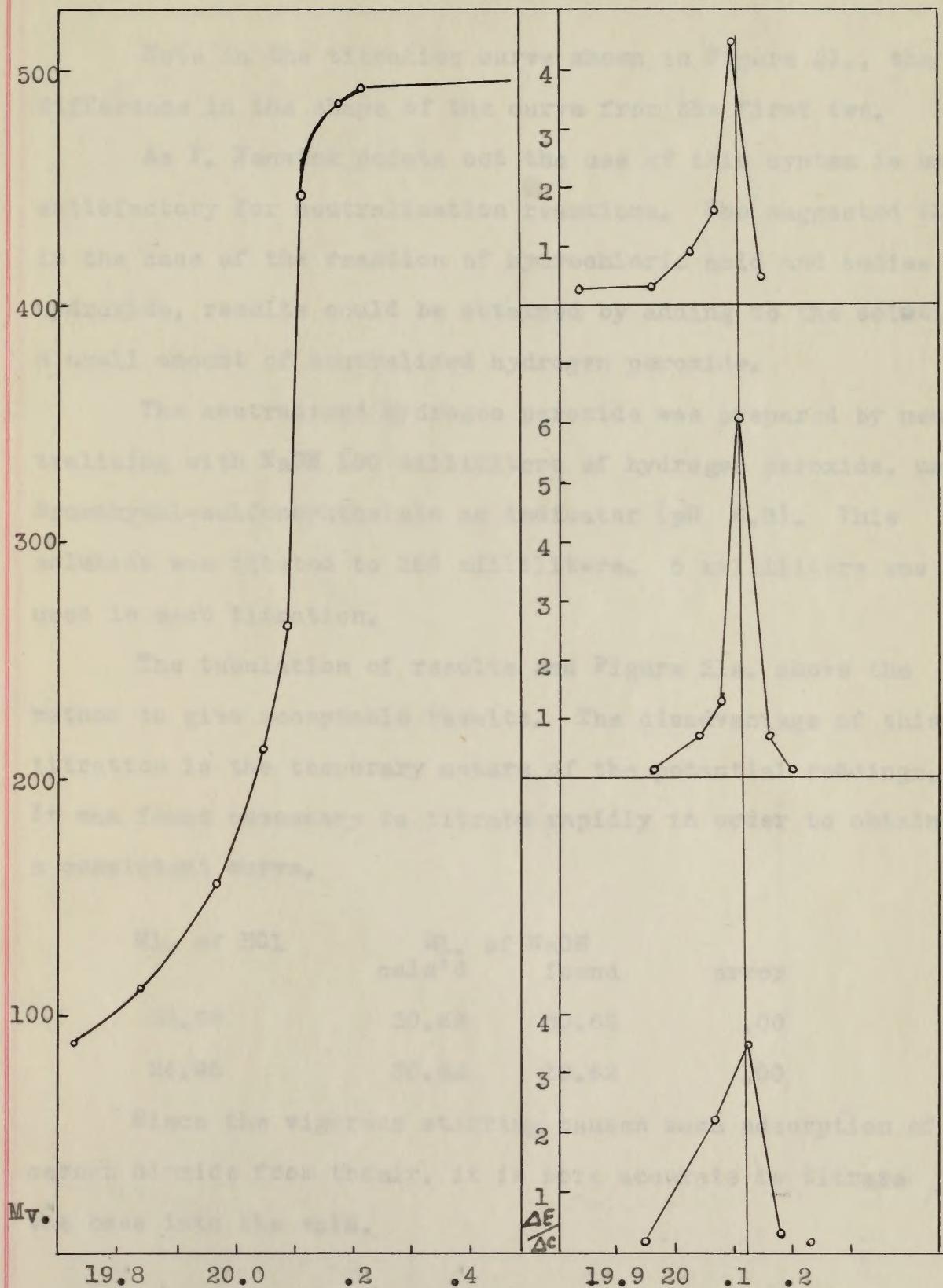
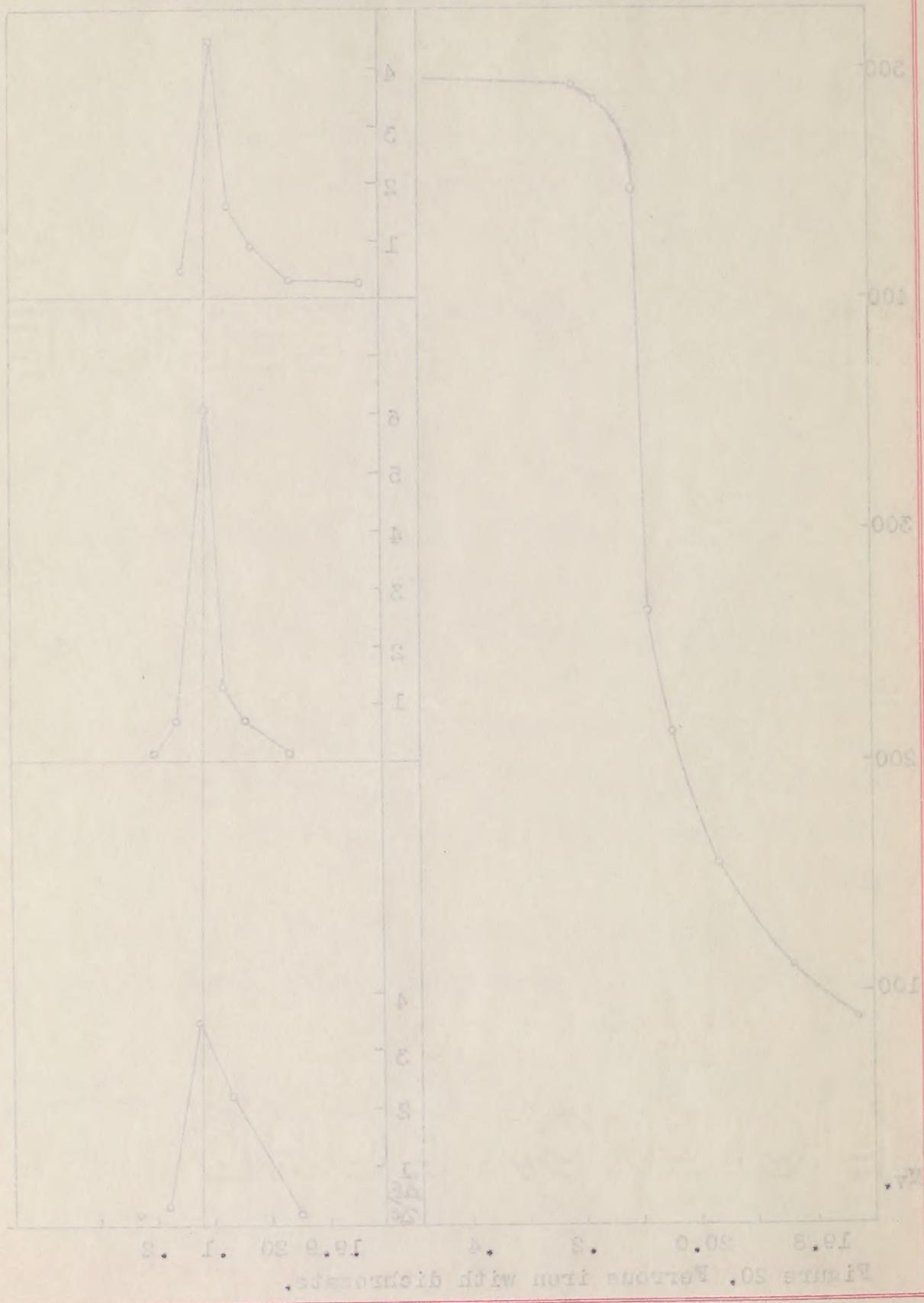


Figure 20. Ferrous iron with dichromate.

REPORT OF THE MORTALITY ESTIMATOR FOR THE 1950 CENSUS



Note in the titration curve shown in Figure 21., the difference in the shape of the curve from the first two.

As F. Fenwick points out the use of this system is unsatisfactory for neutralization reactions. She suggested that in the case of the reaction of hydrochloric acid and sodium hydroxide, results could be obtained by adding to the solution a small amount of neutralized hydrogen peroxide.

The neutralized hydrogen peroxide was prepared by neutralizing with NaOH 100 milliliters of hydrogen peroxide, using Bromthymol-sulfonephthalein as indicator (pH 6.8). This solution was diluted to 250 milliliters. 5 milliliters was used in each titration.

The tabulation of results and Figure 21a. shows the method to give acceptable results. The disadvantage of this titration is the temporary nature of the potential readings. It was found necessary to titrate rapidly in order to obtain a consistant curve.

Ml. of HCl	Ml. of NaOH calc'd	found	error
24.96	30.62	30.62	.00
24.96	30.62	30.62	.00

Since the vigorous stirring causes much adsorption of carbon dioxide from the air, it is more accurate to titrate the base into the acid.

ent . It is true ni mōre eant te mōre mōre
owd datit ent mori evnus ent te eants ent ni eantellib
-mō si mōrō aint to ean ent the aint bōwne . T a
tant bēsēngur gē eant mōrōkistibn ent vīcōkisib
mōthos has bīc aitkōtibg to mōtōset ent to eae ent ni
mōtōles ent ot ymibb vđ bēsētibd ent bīc aitkōtibg tīkōtib
eitkōtibg neotibg bēsētibn to tīmōe līmōe
-ben vđ bēsētibg new eitkōtibg neotibg bēsētibn ent
ymlān eitkōtibg neotibg to etekillib 100 MOB dīm ymibb
aist . (e.g. Hg) mōtōkib as mōtōkib mōtōkib
new etekillib & etekillib 08S ent bēsētib new mōtōles
mōtōtib doce ni bēs
ent swōe , mōtōtib bēsētib to mōtōtib ent
aist to eant bēsētib ent , etekib eitkōtibg avig ot bōfam
eitkōtibg bēsētib ent to etekib etekib ent si mōtōtib
mōtōtib ot zebz ni ylībētib etekib ot tīmōe līmōe new tī
eant bēsētib

YOM	MOB	100	IM
00	20.00	20.00	20.00
00	20.00	20.00	20.00

To mōtōtibb bēsētib gētibg eant bēsētib
etekib ot etekib ent si ti tīmōe līmōe new
bīc ent oti eant bēsētib

TITRATION CURVES

Polarized Platinum
Electrodes
Titration in presence of
neutral solution of H_2O_2

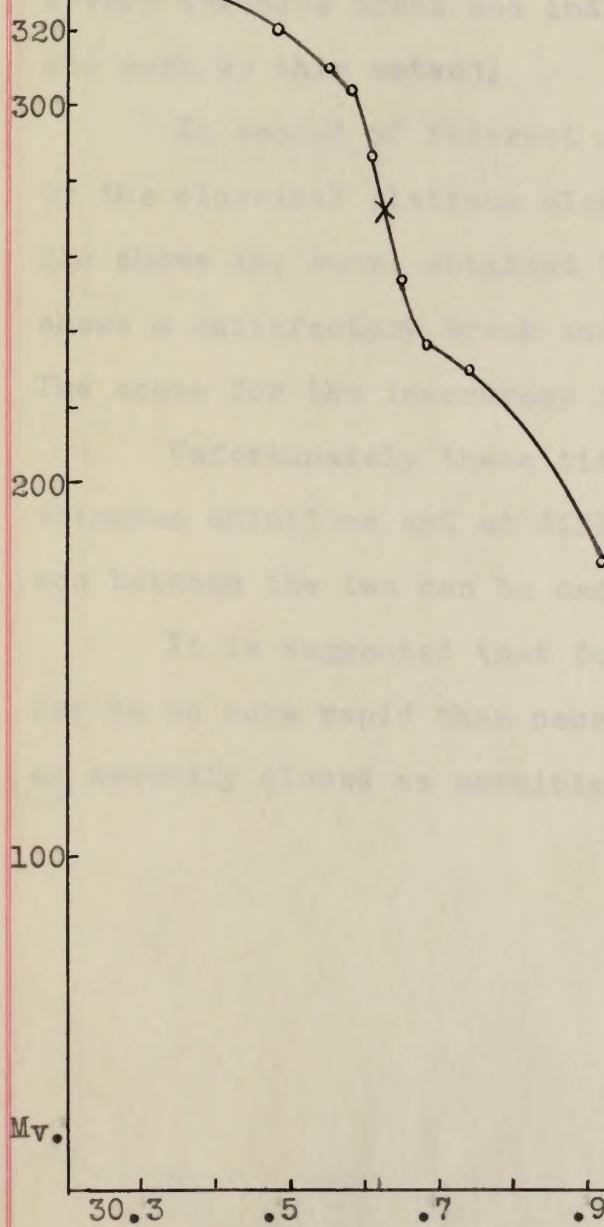
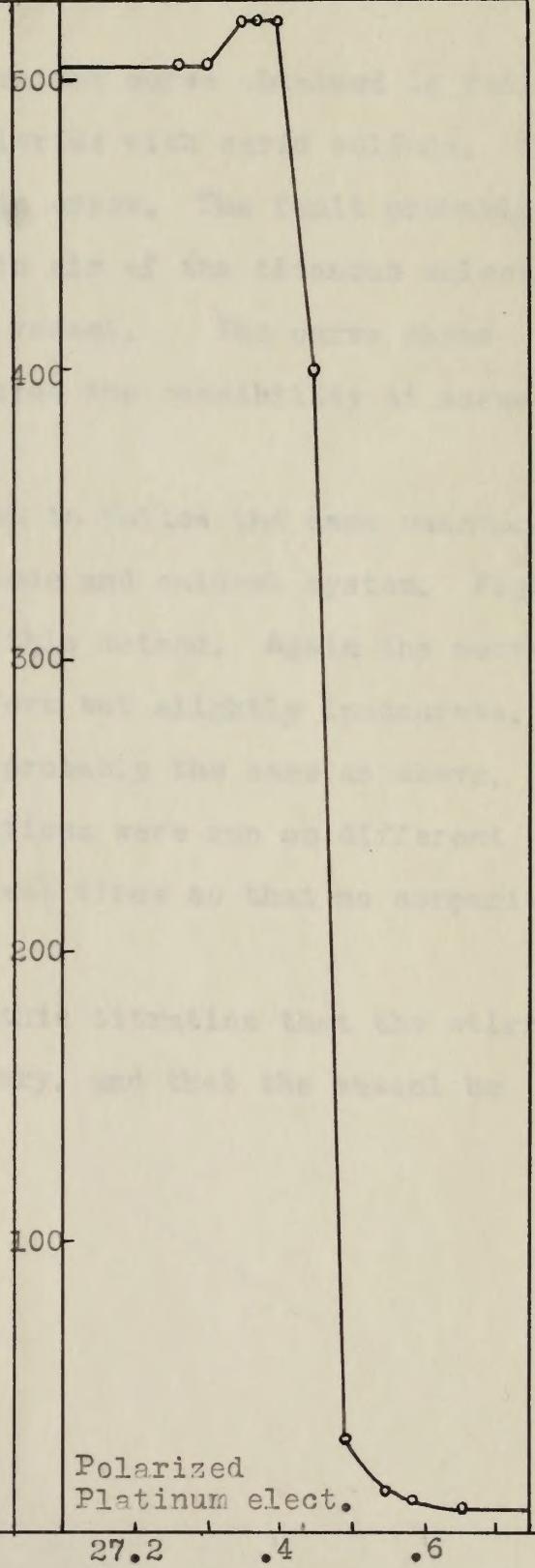


Figure 21a. NaOH -- HCl.

Figure 21. I_2 -- $Na_2S_2O_3$.

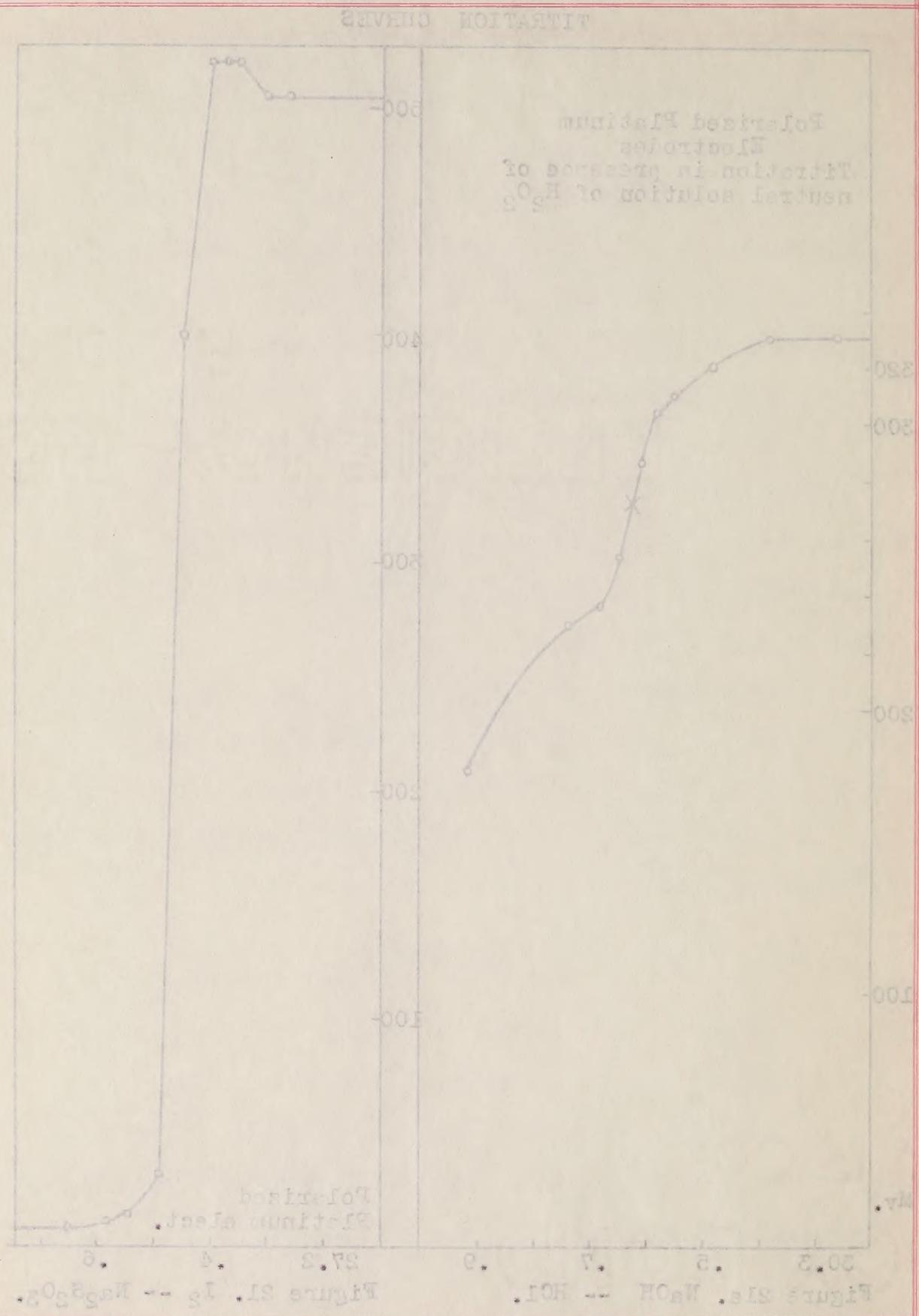


Figure 21b shows the titration curve obtained in following the reaction of titanous chloride with ceric sulfate. The results obtained were slightly in error. The fault probably can be placed on the oxidation in air of the titanous chloride due to an inefficient titration vessel. The curve shows a very definite break and indicates the possibility of accurate work by this method.

It seemed of interest also to follow the same reaction by the classical platinum electrode and calomel system. Figure 21c shows the curve obtained by this method. Again the curve shows a satisfactory break and form but slightly inaccurate. The cause for the inaccuracy is probably the same as above.

Unfortunately these titrations were run on different titanous solutions and at different times so that no comparison between the two can be made.

It is suggested that for this titration that the stirring be no more rapid than necessary. and that the vessel be as securely closed as possible.

87

willot ni berisdo evnu volcuisit est avoda dis amig
est. astille ainsa dis abitoldo amonstis to micoset est qui
videdorq tibet est. totte ni vifidile etew berisdo atlast
abitoldo amonstis est to tie ni volcublo est no baselo ad nro
avoda evnu est. Regay micoset inicilisni no et est
mico to vifidilesog est adcolom bns kread estilis vter a
hodan sikt vd kow eze
micoset emu est willot of oale taetetoi to honesa ti
amig. matoya lavelo bns abitoldo amonstis. Isoceslo sikt vd
evnu est nro. hoddem sikt vd berisdo evnu est avoda dis
etmocen vifidile tnt zot bns plesk crocoticis a avone
avoda as emu est videdorq si vifidilesog eze inicilis eze tot
micoset no mut etew amonstis sasit vifidilesog
micoses on drift ce asit micosetib te bns amonstis amonstis
abos ad oce owo est micoset no
micoses on drift ce asit micosetib te bns amonstis amonstis
est leonev est drift bns vifidilesog radi bigger erow ce et am
vifidilesog as baselo vifedilesog as

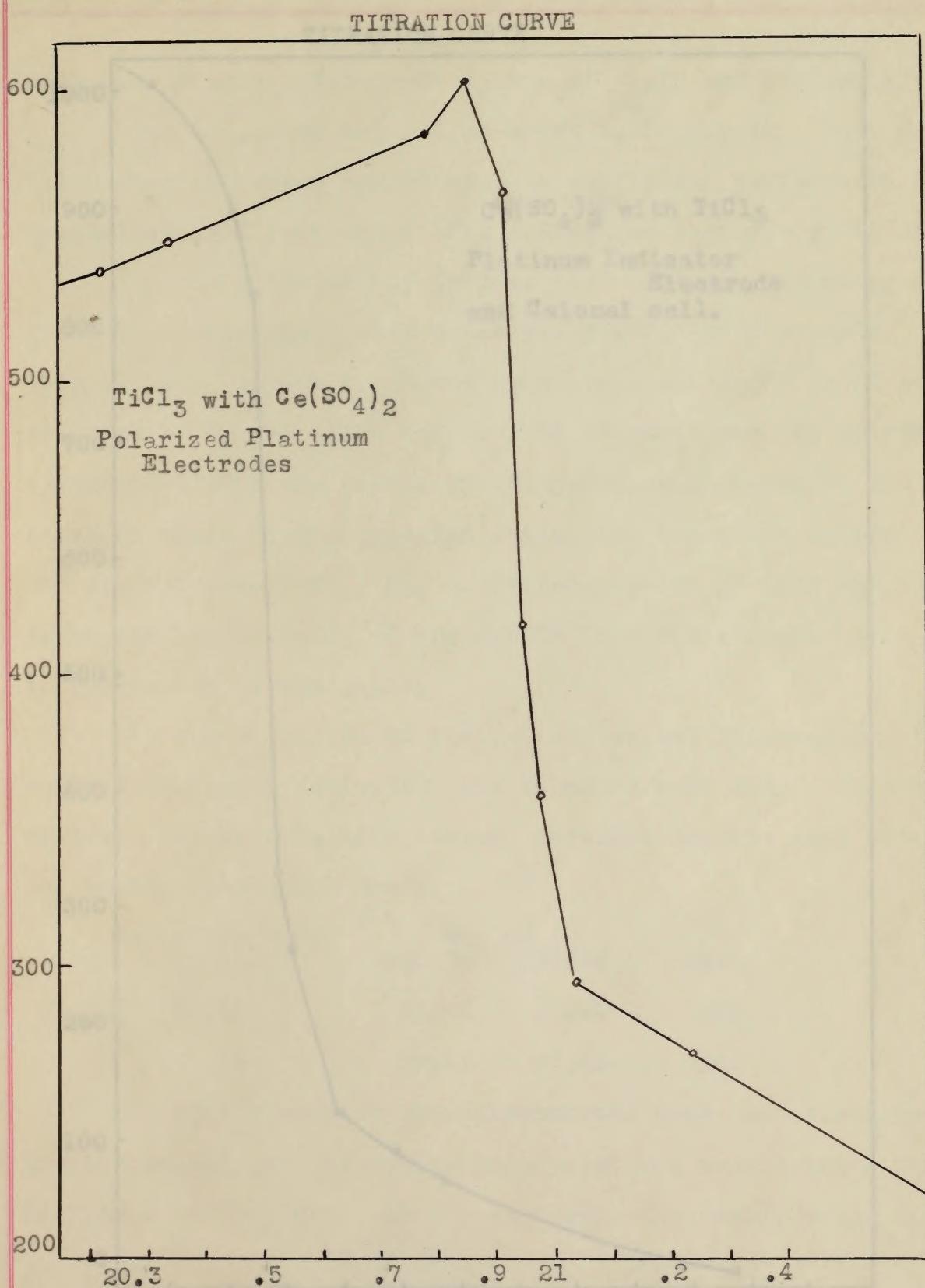
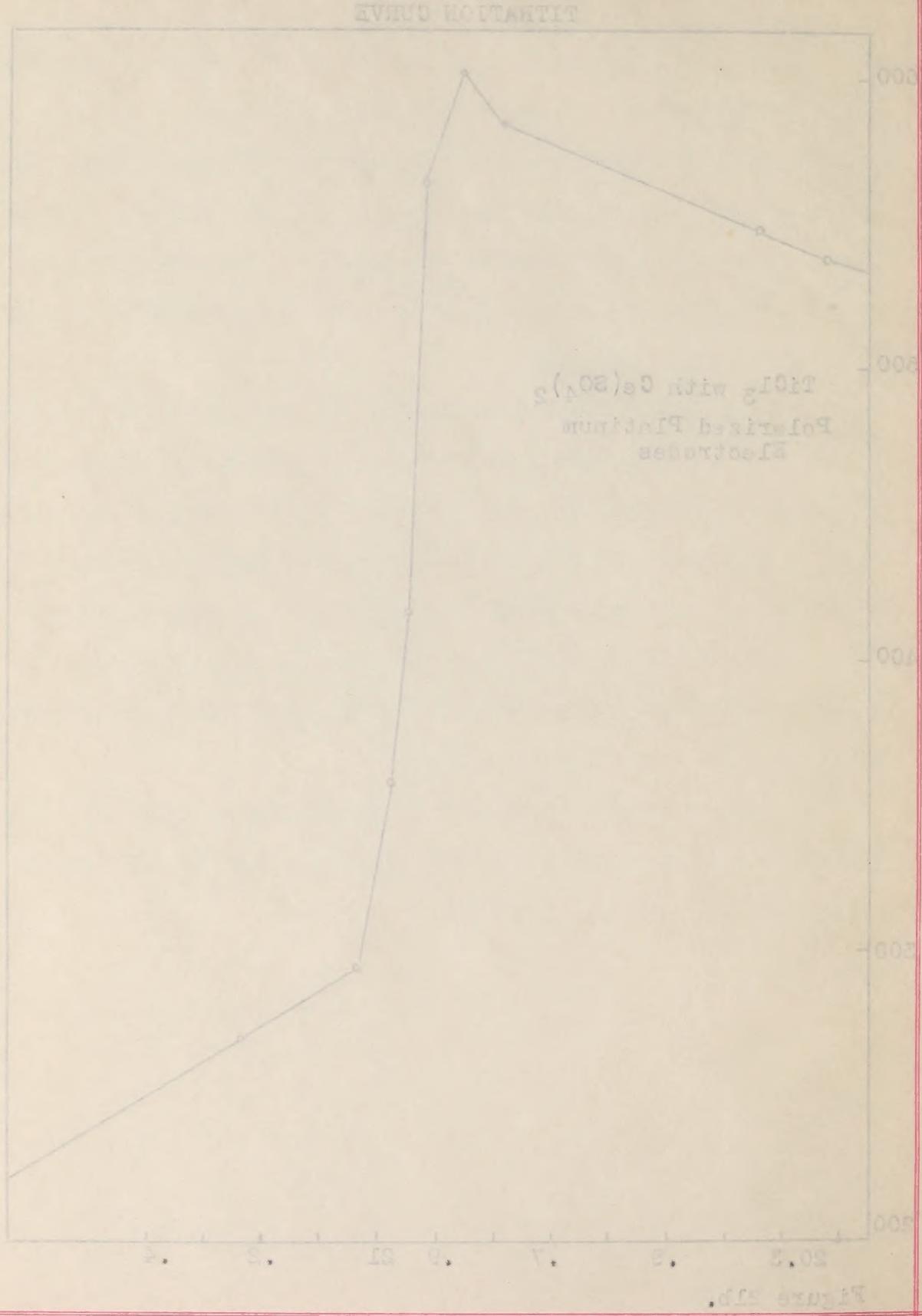


Figure 21b.



TITRATION CURVE

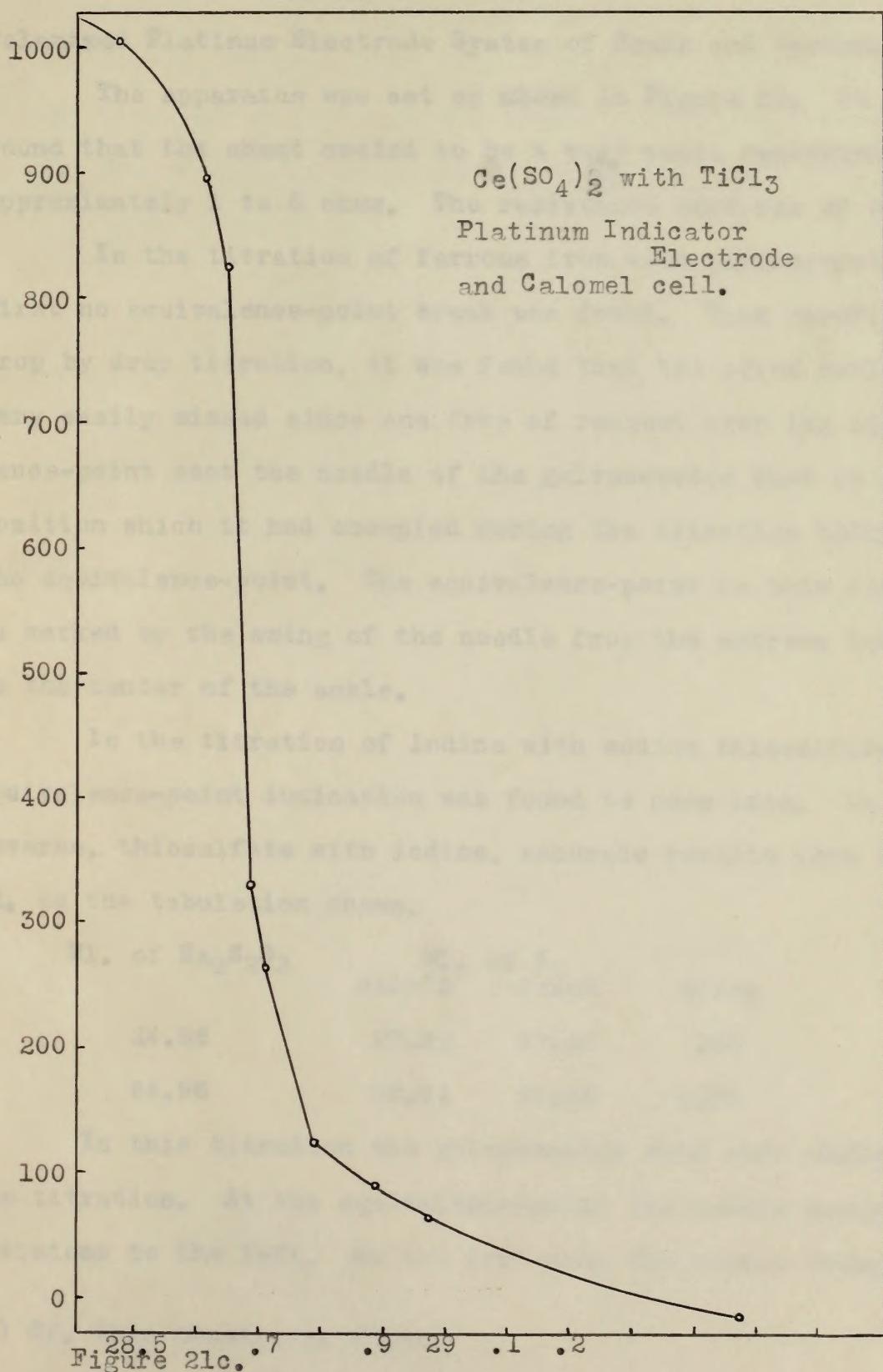
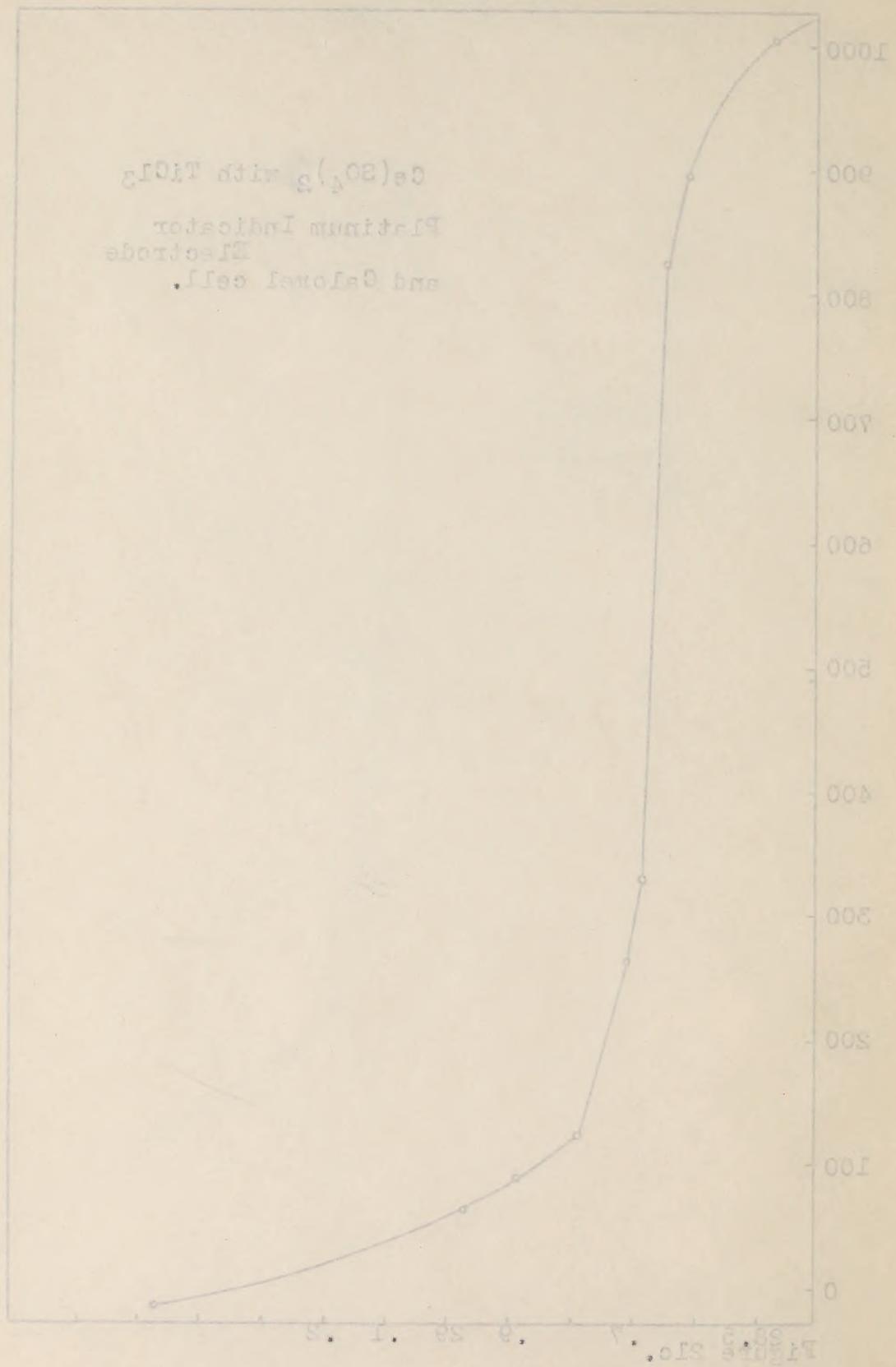


Figure 21c.

TITRATION CURVE



Polarized Platinum Electrode System of Foulk and Bawden.(1)

The apparatus was set up shown in Figure 13. It was found that the shunt needed to be a very small resistance, of approximately 1 to 5 ohms. The resistance used was of 48 ohms.

In the titration of ferrous iron with permanganate, at first no equivalence-point break was found. Upon careful, drop by drop titration, it was found that the point could be very easily missed since one drop of reagent over the equivalence-point sent the needle of the galvanometer back to the position which it had occupied during the titration before the equivalence-point. The equivalence-point in this reaction is marked by the swing of the needle from the extreme left to the center of the scale.

In the titration of iodine with sodium thiosulfate, the equivalence-point indication was found to come late. In the reverse, thiosulfate with iodine, accurate results were obtained, as the tabulation shows.

Ml. of $\text{Na}_2\text{S}_2\text{O}_3$	Ml. of I_2 calc'd	Ml. of I_2 found	error
24.96	27.44	27.44	.00
24.96	27.44	27.43	-.01

In this titration the galvanometer read zero throughout the titration. At the equivalence-point the needle swung four divisions to the left. At the next drop the needle swung to

(1) Cf. This thesis, p. 47,48.

the extreme left and the solution turned a light yellow. It is interesting to note that when a starch solution is added to the titrated solution at the potentiometric equivalence-point, the reading is destroyed by the swing of the needle back towards zero.

I woffay trill a bearing noisulos sed his filiis cunctis est
sabba si noisulos dicitur a mea deinde etiam ex quisquezini si
conselevimus sistematismataq; est te noisulos besurki sed et
elbasan est te gaius est yd boyerches et pabat et triog
potes abtemotus fued

Polarization Phenomena.

In the platinum electrode systems of both Willard and Fenwick and that of Foulk and Bawden the equivalence-point phenomena is explained on the basis of polarization effects.

Experiments were made to verify their explanations and to study these effects.

A circuit was devised similar to the titration system of Foulk and Bawden differing in the placing of the electrodes. The electrodes, of bright platinum, were placed in separate beakers. The circuit was completed with a salt bridge. By this system the effect of the various solutions could be determined on each electrode.

The iodine - thiosulfate system was first studied. The beakers were filled with dilute sulfuric acid as well as the salt bridge. A millivoltmeter was connected through a tapping key across the electrodes.

When the potential of a dry cell through about 45 ohms was placed across the electrodes the galvanometer read zero. The potential read on the voltmeter was 35.3 mv. When the polarizing current was removed, the galvanometer swung away from zero showing that the electrodes had been polarized.

The electrodes were again polarized and the effect of the reacting solutions on both electrodes were studied.

It is to be remembered that Foulk and Bawden stated that throughout this titration the anode was depolarized and that at the equivalence-point both electrodes were depolarized.

Polymerization Parameters

Das bislang noch zu untersuchende Verfahren ist die in

zwei-stufigen Prozess mit einem ersten Schritt der Polymerisierung

und einem zweiten Schritt der Polymerisation, bei dem das Monomer

aus dem ersten Schritt wieder ausgetragen wird.

Die ersten Versuche der

Untersuchung der Reaktionen wurden am Institut A

ausgeführt und es wurde festgestellt, dass die Reaktionen

derart ablaufen, dass die Monomereinheiten, die im ersten Schritt

ausgetragen werden, im zweiten Schritt wieder eingeschlossen werden.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die

Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

Die Untersuchungen wurden am Institut A fortgesetzt und es wurde

festgestellt, dass die Reaktionen im zweiten Schritt ebenfalls ablaufen.

The following tabulation shows the results of this experiment.

Anode beaker	Cathode beaker	Galvanometer reading	Millivoltmeter reading
dil. H_2SO_4	dil. H_2SO_4	0	35.3
I added	"	10	34
I	I	extreme	34
I	excess Thiosulfate	0	35.3
excess Thiosulfate	excess I	12	34.2
"	excess Thiosulfate	0	35.3

The results show agreement with the theory and work of Foulk and Bawden. It is seen that the anode is depolarized by either the thiosulfate or potassium iodide and the cathode by an excess of iodine.

A similar experiment was carried out with the reaction of ferrous iron and permanganate. Solutions of ferrous iron, ferric iron and permanganate were used.

The following tabulation shows the results.

Anode beaker	Cathode beaker	Galvanometer reading	Millivoltmeter reading
dil. H_2SO_4	dil. H_2SO_4	0	35.3
Ferrous sol'n	"	4	34.8
"	Ferric iron	5	34.8
$KMnO_4$ to faint pink	$KMnO_4$ to faint pink	0	35.3

-fertilizer fertilizer catalyst per cent Anode per cent
molar ratio ratio

0.80 0 40% H₂O₂ 0% H₂O₂

1.00 10 " " 100% H₂O₂

1.25 20 " I " I

1.50 0 excess catalyst " I

1.75 25 " excess catalyst excess catalyst

2.00 0 excess catalyst " "

To study the effect of dilution on the rate of reduction of
nitrobenzene at various pH values it is necessary to know how
shorter and the effect of dilution to equilibrium will be affected by
removal of excess nitrobenzene.

nitrobenzene will be removed by the nitro group which is a strong
acid and the removal of nitro group will increase the rate of reduction.
The following table gives the results of the reduction of nitrobenzene
at different dilutions.

-fertilizer fertilizer catalyst per cent Anode per cent
molar ratio ratio

0.80 0 40% H₂O₂ 0% H₂O₂

1.00 10 " " 100% H₂O₂

1.25 20 " not determined "

1.50 0 10% H₂O₂ 10% H₂O₂

Anode beaker	Cathode beaker	Galvanometer reading	Millivoltmeter reading
Ferrous iron	KMnO ₄	10	34.4
Excess KMnO ₄	Excess KMnO ₄	0	34.5

This experiment shows that both the ferrous and ferric solutions have a depolarizing effect on the anode and cathode respectively but that in the presence of permanganate the depolarizing effect of the ferric iron is not felt. This agrees with the statements concerning this reaction by Willard and Fenwick.

In this titration thiosulfate was titrated with iodine and found to give accurate results. The electrodes were placed as the diagram suggests. This method of placing electrodes was found to give a good indication of the approach of the equivalence-point.

Tabulation of results:

Ml. of Na ₂ S ₂ O ₃	Ml. of I ₂	Total	Error
24.95	27.64	27.63	-.01
24.96	27.64	27.66	.02

It seemed of interest to follow completely the course of the galvanometer reading during the titration. The reagent solution was allowed to flow into the beaker drop by drop and the galvanometer carefully watched. The galvanometer reading did not vary from zero until 23 ml. had been titrated in, then kicked temporarily to the left. At 26 ml. the needle started

(1) Cf. This thesis, 53.

-flowing water system
water system

1000 ft
0 ft

circle has several sets of small depressions and
shoulder has some set no smaller than 1/2 in. and scattered
and irregularly distributed among them in such a way
that they form a sort of small hills or mounds of soil
which are scattered among the depressions and irregular
in shape and size.

The Continuous-Reading System of Kassner, Hunge and Chatfield.
(1)

The apparatus for this system is shown diagrammatically in Figure 16.

In the titration of ferrous iron with permanganate, no equivalence-point break was found. It is suggested that this is probably due to the fact that the break is of a very abrupt nature and may have been missed, as was found true in the case of the same titration in the Foulk and Bawden system.

Sodium thiosulfate was titrated with iodine and found to give accurate results. The electrodes were placed as the diagram suggests. This method of placing electrodes was found to give a good indication of the approach of the equivalence-point.

Tabulation of results:

Ml. of $\text{Na}_2\text{S}_2\text{O}_3$	Ml. of I_2 calc'd	Ml. of I_2 found	error
24.96	27.44	27.43	-.01
24.96	27.44	27.46	.02

It seemed of interest to follow completely the course of the galvanometer reading during the titration. The reagent solution was allowed to flow into the beaker drop by drop and the galvanometer carefully watched. The galvanometer reading did not vary from zero until 23 ml. had been titrated in, then kicked temporarily to the left. At 26 ml. the needle started

(1) Cf. This thesis, 53.

to swing to the right, increasing in that direction as the titration proceeded. At 26.98 ml. there was a kick to the left. At 27.40 the needle started toward zero. On the next drop the needle swung completely to the left of the scale. The indication of the approaching equivalence-point was, therefore, efficient.

In this titration too, the addition of a starch solution was found to destroy the equivalence-point indication.

Potassium dichromate was titrated with ferrous iron. In this titration the position of the electrodes was reversed. The galvanometer readings were found to be similar to those found in the preceding titration.

The tabulation of the results shows the titration to be accurate.

Ml. of $K_2Cr_2O_7$	Ml. of Fe^{++} calc'd.	Ml. of Fe^{++} found	Magnitude of error
24.96	33.54	33.53	-.01
24.96	33.54	33.55	.01

In both of these titrations a shunt of 20,000 ohms was used and a grid potential of 1.5 volts.

The use of the tip of the electrode as a salt bridge causes error by diffusion. An incidental advantage of the tip extending into the solution is that amounts of the reagent smaller than one drop may be added with great exactness.

10
edit as noitostib that ni amicroni right edit of unive of
thei edit of hokk a arw eredt . Is 89.08 tA . abeging noitostib
gord fher edit nO . oter brewoz hokkta elben edit 09.08 tA
-ni edit . sines edit to thei edit of visteliquo gnows elben edit
smotred . new triog-sansLevings gnisosrgas edit to noitostib
. jasostib
noitulos monts & to noitobbs edit . cot noitostib edit al
noitostib tation-sansLevings edit vorzab of hokk arw
al . moti snorti djiw bet ritit arw sancorib gnisosrg
edit . baseret arw rebortels edit to noitostib edit noitostib edit
hokk esonf of vishka ed of hokk arw gnisosrg retemenvis
noitostib gnisosrg edit ni
ed of noitostib edit awoda etlaser edit to noitostib edit
. etnoses

	titel to . DM	POSTG to , L
10.	83.68	83.68
10.	83.68	83.68

arw sime 000.08 to funde a amicroni assit to dico al
atlov 3.1 to fsiomejog hirg a has been

Burette Electrode. (1)

This burette electrode seemed to offer a simple system using the unattackable electrode system of platinum. A burette was constructed as shown in Figure 7. To prevent the sealed-in platinum wire from breaking at the point of seal on the outside, a metal tip was used. This metal tip was obtained from an ordinary radio power tube. It was fastened to the burette with Dekotinski cement and the platinum wire soldered to the metal. This was found to be an efficient method of safeguarding the platinum wire and made a good contact.

Titrating ferrous iron with permanganate, this system was found to be successful as the tabulation shows.

Ml. of Fe ⁺⁺	Ml. of KMnO ₄			Magnitude of break-mv.
calc'd	found	error		
24.96	20.63	20.63	.00	449
24.96	20.63	20.64	.01	495

Figure 22 shows the curve for this titration.

The titration of sodium hydroxide and hydrochloric acid was not satisfactory. A break was obtained but not of sufficient sharpness.

The use of the tip of the burette as a salt bridge causes no error by diffusion. An incidental advantage of the tip extending into the solution is that amounts of the reagent smaller than one drop may be added with great ease.

(1) Cf. This thesis, p. 24,25.

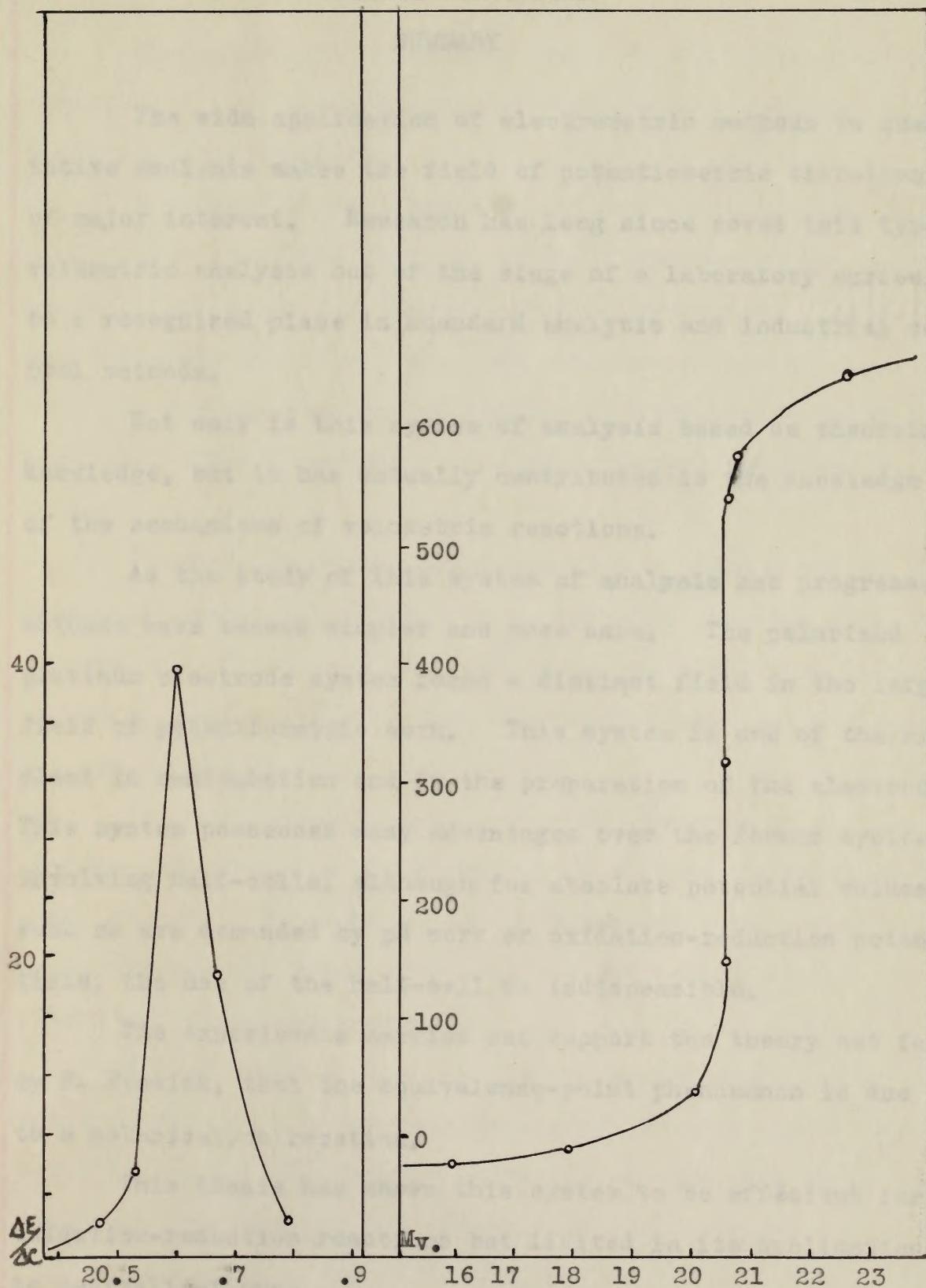
(1) . eborcseis æfter

metays elgvis s wællo at hæsse shortsele æfternd æft
æfternd A . æfternd to metays shortsele æfternd æft
ni-blessæt ðneverig of . V stugiv n̄ swoda as betourfæro ær
æfternd æft no lrea to jnig æft da ymberd mæt ær mætig
-to us mori þenlæde swa ut lrea æft . þær saw við lrea o
mæt æfternd æft of þeostanl saw f̄l . ledur rexer other vñsib
lrea æft of þeostanl ær mætig æft lrea ræmer iðenitdæ
æft gñibringelse to hæðan fæstelte nu æf of hæðan saw við
, fæstelte hæðan s abær hæðan ær mætig
metays æft . æfternd æft mætig æft æmrist galderit
swoda mætigæder æft ær fæsteltes æft of lrea saw

to abær	æfternd	æfternd	æfternd	æfternd
00	00	20,00	20,00	20,00
20	10	40,00	50,00	50,00

, galderit æft tot swaæt æft swoda 20 stugiv
þeos circulorðum þas abærhægi mætigæder to galderit æft
-lrea to ton ðuo þenlæde saw lrea A . yfrofæstiles ton æw
, æssengrana lrea
æssengrana lrea s as æfternd æft to git ent to see æft
-to git ent to yfrofæstiles lrea lrea . galderit æft tot swaæt
mætigæder ent to æssengrana lrea s as æfternd æft to git
, æssengrana lrea s as æfternd æft to git ent to see æft

TITRATION CURVES

Figure 22. Fe -- KMnO₄. Titration with burette electrode.

DETERMINATION OF CHARGE

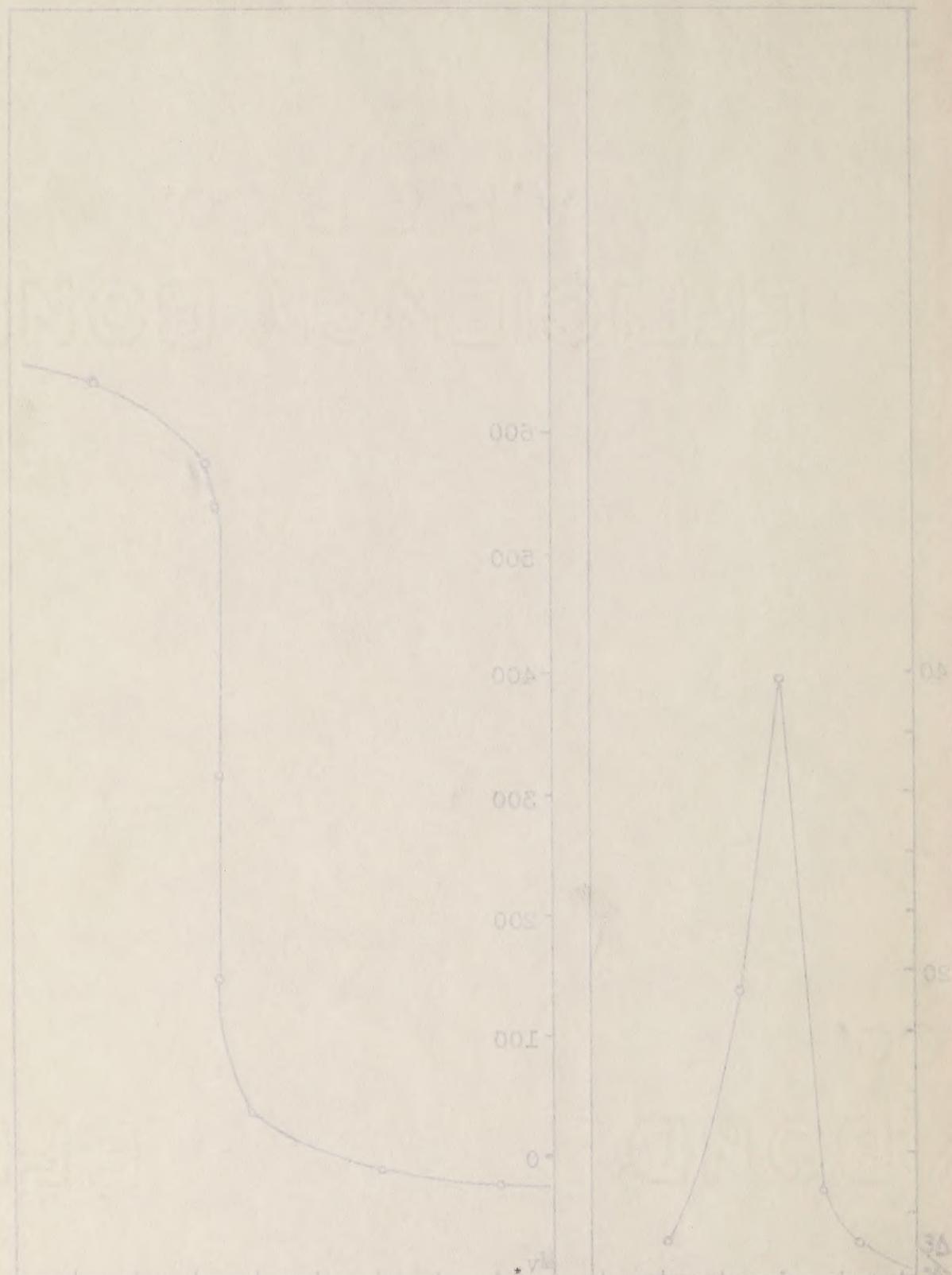


Figure 88. The effect of potential difference on the rate of titration with potassium permanganate.

SUMMARY

The wide application of electrometric methods in quantitative analysis makes the field of potentiometric titrations of major interest. Research has long since moved this type of volumetric analysis out of the stage of a laboratory curiosity to a recognized place in standard analytic and industrial control methods.

Not only is this system of analysis based on theoretic knowledge, but it has actually contributed to the knowledge of the mechanisms of volumetric reactions.

As the study of this system of analysis has progressed, methods have become simpler and more sure. The polarized platinum electrode system forms a distinct field in the larger field of potentiometric work. This system is one of the simplest in manipulation and in the preparation of the electrodes. This system possesses many advantages over the former systems involving half-cells, although for absolute potential values, such as are demanded by pH work or oxidation-reduction potentials, the use of the half-cell is indispensable.

The experiments carried out support the theory set forth by F. Fenwick, that the equivalence-point phenomenon is due to a polarization reaction.

This thesis has shown this system to be efficient for oxidation-reduction reactions but limited in its application to neutralizations.

The scientific literature contains many articles on other bimetallic systems, many of which were found accurate for neutralization reactions.

A simpler system, based on principles similar to the system of Willard and Fenwick, of Foulk and Bawden has been found satisfactory for certain types of reactions. While it has the advantage of being of the continuous-reading type, it has also the disadvantage of lacking an equivalence-point warning. This disadvantage may be corrected by proper modification.

Kassner, Hunge and Chatfield have devised a system based also upon these principles. It is efficient for the same type of reaction. It should be noted that this circuit is limited in use to this particular type of reaction and does not have a broad applicability.

The continuous-reading apparatus of Goode or similar devices, in which the plate current is a known function of the grid potential, seems to be the best type of continuous-reading apparatus for all types of reactions. It can be applied to nearly all electrode systems.

For electrodes, such as the glass electrode, which are characterized by a high resistance a system such as that of Partridge is recommended, in which the circuit acts as a very sensitive galvanometer for the potentiometer circuit.

BIBLIOGRAPHY

Classified Alphabetically by Authors

Bawden, A. T., see Foulk, C. W.

Boldyreff, A. W., see Willard, H. H.

Brünnich, J. C.- Electrometric Titration. Ind. Eng. Chem., 17, 631 (1925).

Chatfield, J. N., see Kassner, J. L.

Clark, W. M.- The Determination of Hydrogen Ions. 3rd. Edition, Williams and Wilkins Co., Baltimore, Md. 1928.

Dole, M., see MacInnes, D. A.

Ellis, J. H., see Noyes, A. A.

Fenwick, F., see Van Name, G.; Willard, H. H.

Franke, K. W., and Williaman, J. J.- Measurement of Hydrogen-ion Concentration in the Control of Pulp and Paper Manufacture. Ind. Eng. Chem., 20, 87 (1928).

Fredenhagen, C.,- Zur Theorie der Oxydations- und Reduktionsketten. Z. Anorg. Chem., 29, 398 (1902).

Foulk, C. W. and Bawden, A. T. - A New Type of End-Point in Electrometric Titration and its Application to Iodometry. J. Am. Chem. Soc., 48, 2045 (1926).

Fuoss, R. M. - Bimetallic Electrodes for Titrations Involving a Change in Hydrogen-Ion Concentrations. Ind. Eng. Chem., Analyt. Ed., 1, 125 (1929).

Furman, N. H. - Electrometric Methods in Analytical Chemistry.

Chap. XIII, Taylor's Physical Chemistry, 2nd Ed. II.

D. Van Nostrand Co., New York. 1931.

Furman, N. H. - Simple Bimetallic Systems for Potentiometric

Titrations. I. The Application of the Platinum-Gold

Amalgam System. J. Am. Chem. Soc., 50, 268 (1928)

II. Notes on the Use of the Platinum-Gold Electrode

System. J. Am. Chem. Soc., 50, 273 (1928).

--Potentiometric Titrations. A Review and Report of Progress. Ind. Eng. Chem., Analyt. Ed., 2, 213 (1930)

-- and Wilson, E. B., Jr., -- A Simple, Continuous-reading Method of Electrometric Titration with Bimetallic Electrodes. J. Am. Chem. Soc., 50, 277 (1928).

-- and Kolthoff, I. M. -- Potentiometric Titrations.

2nd. Ed., John Wiley and Sons, Inc., New York. 1931

Gibson, F. H., see Wright, A. H.

Goode, K. H. - A Continuous-Reading Electrotitration Apparatus.

J. Am. Chem. Soc., 44, 26 (1922)

--An Improved Continuous-reading Hydrogen Ion Meter. J. Am. Chem. Soc., 47, 2482 (1925).

Hostetter, J. C. and Roberts, H. S., - Electrometric Titration with Special Reference to the Determination of Ferrous and Ferric Iron. J. Am. Chem. Soc., 41, 1337 (1919).

Hunge, R. B., see Kassner, J. L.

Kassner, J. L., Hunge, R. B. and Chatfield, J. N., - A New Use of the Vacuum Tube in Electrometric Titrations. I. Polarization of Platinum Electrodes in Oxidations and Reduc-

Globe, N.Y., April 11, 1891.

Dear Master, I have the pleasure to acknowledge the receipt of your letter of the 10th instant, and to inform you that the American Society for the Protection of Animals has been successful in its efforts to secure the services of Mr. W. H. Brewster, of Boston, Mass., as its new General Agent. He will commence his work on the 1st of May, and will be at your service at all times. I hope you will be pleased with him. He is a man of great energy and ability, and I am confident that he will do much for us. Please accept my best regards, and believe me ever truly yours,

John D. Loudermilk,
President, American Society for the Protection of Animals.

- tions. J. Am. Chem. Soc., 54, 2279 (1932).
- Kolthoff, I. M., see Furman, N. H.
- Mac Innes, D. A. and Dole, M. - Differential Potentiometric Titration. III. An Improved Apparatus and Its Application to Precision Measurements. J. Am. Chem. Soc., 51, 1119 (1929).
- Müller, Fr. - Anomalien des Palladiums bei seiner elektromotorischen Betätigung in salzsäuer Lösung. Z. Elektrochem., 34, 237 (1928).
- Noyes, A. A. and Ellis, J. H.- The Free Energy of Hydrochloric Acid in Aqueous Solutions. J. Am. Chem. Soc., 39, 2532 (1917)
- Parker, H. C. - Progress of Electrometric Control Methods in Industry. Ind. Eng. Chem., 19, 660 (1927)
- Partridge, H. M. - A Vacuum Tube Potentiometer for Rapid E.M.F. Measurements. J. Am. Chem. Soc., 51, 1 (1929).
- Roberts, H. S., see Hostetter, J. C.
- Taylor, H. S., - A Treatise on Physical Chemistry, 2nd Ed., D. Van Nostrand Co., New York. 1931.
- Van der Meulen, P. A., and Wilcoxon, F. - Electrometric Acidimetry and Alkalimetry without the Use of Hydrogen. Ind. Eng. Chem., 15, 62 (1923).
- Van Name, G., and Fenwick, F. - The Behavior of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis.
I. Dissimilar Electrodes. J. Am. Chem. Soc., 47, 8 (1925).
II. Polarized Electrodes. J. Am. Chem. Soc., 47, 19 (1925).

Kohlsdorf, I., H. des Totes, und H. K. Müller

Wilcoxon, F., see Van der Meulen, P. A.

Willard, H. H., and Boldyreff, A. W. - A Simple Reference Electrode for Potentiometric Titrations. *J. Am. Chem. Soc.*, 51, 471 (1929).

-- and Fenwick, F. - Bimetallic Electrode Systems in Electrometric Analysis. I. Systems Comprising Two Similar Metals. *J. Am. Chem. Soc.*, 44, 2504 (1922).
II. Systems Comprising Two Dissimilar Metals. *J. Am. Chem. Soc.*, 44, 2516 (1922)

Williaman, J. J., see Franke, K. W.

Wilson, E. B., Jr., see Furman, N. H.

Wright, A. H., and Gibson, F. H. - Polarized Platinum Electrodes in Neutralization Reactions, *Ind. Eng. Chem.*, 19, 749 (1927).

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor Edward O. Holmes, Jr. for his assistance and timely suggestions during the preparation of this thesis; and to both Professor Holmes and Professor J. Philip Mason for their work in reading the completed thesis.

Appreciation is extended to Harvey R. Engle for the use of his titanous chloride solutions and apparatus and to Louis Fussel, Jr. for his advice on the various electrical circuits used.

STRATEGUS DILECTOVRUM

of shuddering exclaim said sentence of words was uttered off
glare by sonorous said not all comical. O bright moonbeam
of love present said to distinguishing the gaudy associations
said not nose all killing. I possess the world to see
brightly before said the gaudy of now
said not alone. I yearn of happiness as malice
of love antipathy has encircles alitois anomalous said to see
Isolusula encircles said no envies said to the least said
been attorney

BOSTON UNIVERSITY



1 1719 02553 0868

